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# RESEARCH MEMORANDUM

## SOME FUNDAMENTAL ASPECTS OF NITRIC ACID OXIDANTS FOR ROCKET APPLICATIONS

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## SUMMARY

The literature pertaining to the preparation, physical properties, corrosiveness, thermal stability, constitution, and analysis of various nitric acids is reviewed primarily with respect to their use as rocket oxidants. Conflicting data are evaluated and recommendations for additional experimental work are indicated.

Reactions of nitric acid which could occur during the starting and steady-stage phases of rocket operation are discussed and probable mechanisms are selected on the basis of reported thermal and kinetic data.

## INTRODUCTION

Concentrated nitric acids containing at least 90 percent nitric acid and oxides of nitrogen are used widely as rocket propellants; hence, the properties and the behavior of these acids are of considerable interest to the rocket engineer. Because the recent literature in this field of nitric acid chemistry is quite scattered, it was felt that a critical survey of available information would accomplish two purposes: (1) the present state of knowledge of the chemistry of nitric acid pertinent to rocket technology would be available in compact form, and (2) the areas in which additional or continuing experimental work is required would become apparent.

Accordingly, a search of the literature on nitric acid was conducted at the NACA Lewis laboratory from August 1951 to March 1952 and the results are reported herein.

Subjects covered include commercial and laboratory preparations, physical properties, corrosion, thermal stability, constitution, and analysis. Where conflicting data have been reported, an attempt was made to select the most reliable values.

The reactions which could occur in a rocket engine are discussed and probable mechanisms are selected on the basis of reported thermal and kinetic data.

## PREPARATION AND PROPERTIES

### Commercial Manufacture

Methods that have been used or proposed for the commerical production of nitric acid may be divided as follows: (1) oxidation of ammonia, (2) production from saltpeter, and (3) direct fixation of nitrogen as oxide.

General descriptions of the several methods for the manufacture of nitric acid will be found in references 1 to 4, and bibliographies and synopses of publications and patents from 1932 to 1941 bearing on its manufacture are contained in references 5 and 6.

Ammonia oxidation. - In the United States, 90 percent of the nitric acid produced is made by the oxidation of ammonia (reference 4). A flow sheet of this process is shown by figure 1. The reactions are as follows:

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O \quad (1)$$

$$2NO + O_2 \longrightarrow 2NO_2 \quad (2)$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \quad (3)$$

Ammonia is oxidized by air on platinum screens packed in layers of 10 to 30 sheets in the reactor. With the newer reactors, the oxidation is carried out at about 750° C and under a pressure of about 100 pounds per square inch; this permits the use of smaller equipment, increases reaction rates, and produces higher-strength acids than was formerly possible at atmospheric pressure.

Production from saltpeter. - At the present time, only 10 percent of the nitric acid produced in the United States is manufactured from saltpeter (reference 4), a distillation being made from a mixture of concentrated sulfuric acid and sodium nitrate in cast-iron retorts:

$$NaNO_3 + H_2SO_4 \longrightarrow HNO_3 + NaHSO_4 \quad (4)$$

A discussion of the technology is contained in reference 7.

Direct fixation of nitrogen as oxide. - At high temperatures, the following equilibrium is shifted toward the right and the reaction rate is rapid:

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (5)$$

This permits the fixation of nitrogen in air as nitric oxide, provided that the gases can be chilled rapidly enough so that the reverse reaction does not take place during the cooling interval. This can be accomplished, for example, by passing air through an electric arc, a method which has been used commercially in European areas where electric power is relatively inexpensive. The electric arc process, however, is uneconomical in the United States.

A new process incorporating refractory pebble beds (reference 8) has attracted considerable interest in this country because it offers promise of economical commercial production of nitric acid by direct fixation of atmospheric nitrogen. A schematic sketch of the apparatus is shown by figure 2. Air under pressure passes through a four-way valve into chamber A containing a high-temperature refractory pebble bed which heats the air to approximately 1800° C. The hot air is then mixed with natural gas which is burned at the top of chamber B increasing the temperature to 2100° C. At this temperature, about 2.5 percent NO is theoretically possible. The gas mixture is then rapidly cooled in the pebble bed of chamber B and about 1 to 2 percent of nitric oxide remains in the exhaust gas. The flow is alternated between the two chambers; in the next cycle, the pebbles in B heat the air and the pebbles in A cool the gas. With the use of this regenerative heating cycle, high temperatures are obtained and the heating costs are lower than if electric energy were used.

Concentration of nitric acid. - Acids with $HNO_3$ concentration as high as 99 percent by weight may be produced by the saltpeter distillation process. Acids from absorption towers used in the ammonia oxidation process and from auxiliary absorption towers used in the saltpeter distillation process have a concentration of only 60 to 70 percent. Acids of this strength may be concentrated by contacting the vapor in a tower with concentrated sulfuric acid (reference 4).

Economics. - Over the period 1929 to 1949, the price of nitric acid remained stable at about $100 per ton of 100-percent acid (reference 4). The high current commercial production of nitric acid of approximately 1,200,000 tons a year (as 100 percent) is a result of greatly increased agricultural and industrial demands and of shortages of sulfuric acid for which nitric acid is often a substitute (fig. 3). The rapid increase in commercial production after the war was facilitated by private acquisitions of government surplus equipment. In 1950, total production

capacity including Army Ordnance stand-by facilities was about 3,660,000 tons per year on a 100-percent-acid basis (reference 9) of which approximately 68 percent could be produced as oxidizer nitric acid (>95 percent $HNO_3$) (reference 9). In order to activate stand-by equipment, considerable amounts of labor and materials would be required (reference 10). Even with all present available equipment in use, it is expected that demand will exceed supply in a war emergency (reference 9); hence, large quantities of nitric acid for rocket propulsion must come from new facilities or a reduction of the supply available for other uses.

Material requirements for the production of 1 ton of nitric acid (as 100 percent) are as follows (reference 4):

| | |
|---|---|
| Ammonia oxidation, 93-95 percent yield: | |
| Anhydrous ammonia, ton | 0.288 |
| Platinum, oz | 0.01-0.02 |
| Air, cu ft | 115,000 |
| Saltpeter distillation, 95-97 percent yield: | |
| Sodium nitrate (96 percent), ton | 1.465 |
| Sulfuric acid (93.2 percent), ton | 1.575 |

## Laboratory Purification

For laboratory experiments, nitric acid assaying more than 99 percent has been prepared by several investigators. Purification requires the removal of (1) water; (2) oxides of nitrogen; (3) other volatile impurities, such as hydrogen chloride and possibly sulfur trioxide; and (4) nonvolatile matter. The usual procedure and the one which appears most reliable is the repeated distillation of nitric acid (two to four times) under reduced pressure (20-30 mm of Hg) from a 1:1 or 1:2 mixture by volume of concentrated nitric acid and concentrated sulfuric acid in an all-glass apparatus protected from light (references 1, 2, 11 to 17). If necessary, the nitric acid is blown with dry air prior to distillation to remove oxides of nitrogen. This is done before distillation because nitrogen tetroxide cannot be removed from highly concentrated nitric acid by this method (references 16 and 18). According to reference 13, nitrogen tetroxide is removed from 62-percent acid by twice distilling from urea at 30 to 40 millimeters of mercury. Complete removal of nitrogen tetroxide prior to distillation apparently is unnecessary because the sulfuric acid combines with nitrogen tetroxide to form "nitrosyl sulfuric acid" (nitrosonium hydrogen sulfate):

$$H_2SO_4 + N_2O_4 \longrightarrow NOHSO_4 + HNO_3 \qquad (6)$$

Absolute nitric acid is unstable at room temperatures and therefore should be crystallized and stored in the dark below -41° F. If the acid is concentrated from chemically pure stock, no trouble should be expected from hydrochloric acid; and if the distillation is conducted carefully, no sulfuric acid will be found in the distillate. If these acids are present, however, addition of barium and silver nitrates with subsequent distillation at reduced pressures will remove them (reference 11).

Other methods have also been used to prepare absolute nitric acid. According to reference 18, 99.7 to 99.8 percent acid was obtained by fractional crystallization. This acid was said to be colored upon melting, however. Absolute nitric acid has been prepared also by adding a calculated quantity of water to nitrogen pentoxide (reference 1).

## Physical Properties

Nitric acids containing less than about 10 percent water by weight are often called fuming. White fuming nitric acid (WFNA) contains only small amounts of nitrogen dioxide, usually less than 1 percent by weight. Red fuming nitric acid (RFNA) contains larger amounts of $NO_2$, 6.5 to 20 percent by weight or more. Mixed acids are solutions of nitric acid, sulfuric acid, and water.

Some physical properties of primary interest to a designer of rocket engines are melting points, boiling points, vapor pressures, vapor compositions, densities, viscosities, thermodynamic functions, and thermal conductivities. Electrolytic conductance is also of interest with respect to analysis and corrosion. Selected values from published data for these properties are presented herein for the following systems: (1) nitric acid and water; (2) nitric acid, nitrogen tetroxide, and water; and (3) nitric acid, sulfuric acid, and water. Other compilations of various physical properties of nitric acid and systems containing nitric acid may be found in references 1 to 3, 7, 19, 20, and 21.

Melting points. - According to reference 22, the melting point of pure nitric acid is -41.59° C. Lower melting points result when nitric acid is a solvent for other substances. A phase diagram for the nitric acid and water system constructed primarily from melting-point data of references 22, 23, and 24 is shown by figure 4(a).

The data indicate the existence of the hydrates $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$ at 77.8 and 53.8 percent by weight $HNO_3$, respectively. The most probable melting points of these hydrates are -37.62° and -18.47° C, respectively, (reference 22). The composition of 90 percent nitric acid and 10 percent water forms a eutectic melting at approximately -65° C.

A phase diagram (reference 25) for the system nitric acid and nitrogen tetroxide is shown by figure 4(b). According to these data, a eutectic melting at -73° C exists at 18 percent by weight nitrogen tetroxide in nitric acid. The melting point then increases with increasing amounts of nitrogen tetroxide. At about 50 percent and above the melting point of approximately -11° C, the solution exists in two liquid layers. These data indicate that red fuming nitric acids containing approximately 18 percent nitrogen tetroxide may be suitable for low-temperature applications. A few experiments made at this laboratory, however, indicate that the eutectic mixture of red fuming nitric acid melts higher than -73° C. It is desirable that the data of reference 25 be corroborated by further experimental melting-point determinations of nitric acids containing 0 to 50 percent nitrogen tetroxide. Experimental melting-point determinations for the system nitric acid, nitrogen tetroxide, and water, especially in the regions of high nitric acid content, are also desirable.

Melting-point data for the ternary system nitric acid, sulfuric acid, and water are reported (reference 26). A phase diagram describing approximately the projected melting surface of this system in the region 50 to 100 percent nitric acid was constructed from these data and is shown by figure 5. The solid lines are isotherms and the broken lines indicate eutectic compositions. The following materials freeze out in the regions designated: $HNO_3$, $HNO_3 \cdot H_2O$, $HNO_3 \cdot 3H_2O$, and $H_2SO_4 \cdot H_2O$. These data show a eutectic line for mixed acids containing about 12 percent water and 0 to 30 percent sulfuric acid; at approximately 30 percent sulfuric acid and 0 to 17 percent water, another eutectic line occurs. The characteristics of the approximate region 0 to 3 percent water, 29 to 35 percent sulfuric acid are not well defined by these data probably because glasses form which make melting-point determinations difficult.

Vapor pressures and boiling points. - Vapor pressure-temperature data for the system nitric acid and water published prior to 1925 are reviewed in reference 29 and tables of smoothed values (appearing also in reference 19) are presented. These data for compositions greater than 70 percent nitric acid, according to the author, were less precise than the data for the more dilute acids. More recent data for concentrated nitric acids are available in references 16, 27, and 28. The total vapor pressures for 100-percent nitric acid reported in these references agree well with calculated fugacities reported in reference 30. A plot of smoothed total and partial pressures for 50- to 100-percent nitric acids based on the data of references 16 and 27 to 30 are presented in figure 6; the smoothed curves deviate somewhat from the data of references 19 and 29. The reported vapor pressures for 80-percent nitric acid are more poorly corroborated than those reported for other compositions; at lower temperatures, the data of reference 16 are used as a compromise.

Reliability of experimentally determined partial pressures reported to date for the nitric acid and water system have been questioned in reference 22. The partial pressures of water and nitric acid at 20° C given in reference 16 were recalculated in reference 22 by the Duhem equation and were found to decrease at low concentrations more rapidly than the reported data indicate. These recalculated values at 20° C are shown also in figure 6. It is to be conceded that the experimental partial pressures are less realistic than the total pressures. The data of figure 6 are idealized in that they represent equilibrium vapor pressures which, for concentrated acids at high temperatures, would be difficult to realize because of the rapid decomposition of the acid to form nitrogen dioxide and oxygen. This phenomenon is discussed in the section entitled "Thermal Stability".

Total vapor pressures for the ternary system nitric acid, nitrogen tetroxide, and water (red fuming nitric acids) are available in reference 28 for the temperatures 0°, 12.5°, and 25° C. The data are reported for anhydrous, 19 N, and 16 N nitric acids diluted with varying amounts of nitrogen tetroxide. The concentrations of the 19 N and 16 N acids were assumed to be 82 and 71 percent by weight, respectively, and triangular diagrams were constructed (fig. 7) showing constant-vapor-pressure lines as functions of composition at 0° and 25° C. These data illustrate the fact that the solubility of nitrogen tetroxide in nitric acid decreases with increased water content.

Data of reference 28 for binary mixtures of nitric acid and nitrogen tetroxide are linear on log p against 1/T plots, but the extrapolated data indicate higher boiling points than are reported in reference 19:

| Nitric acid in nitric acid, nitrogen tetroxide mixture (percent by wt) | Boiling point, °C | |
|---|---|---|
| | Reference 19 | Extrapolated from data of reference 28 |
| 72.9 | 33.0 | 50 |
| 89.0 | 55.0 | 67 |
| 94.9 | 65.0 | 77 |
| 100.0 | 78.5 | 84 |

A need is evident for more vapor-pressure data for the nitric acid, nitrogen tetroxide, and water system, especially at higher temperatures.

A ternary diagram of constant-vapor-pressure lines at 25° C as functions of composition in the system nitric acid, sulfuric acid, and water (reference 19) is shown by figure 8(a). Constant-boiling-point

lines at 760 millimeters of mercury are shown for the same system by figure 8(b) (reference 19). Somewhat similar data are reported in reference 31. Lines of constant vapor composition for the system at 760 millimeters of mercury compiled from several sources (reference 19) are shown by figure 8(c). Additional triangular plots of boiling points and vapor compositions at several subatmospheric pressures, derived from data of reference 32, are available in reference 19.

Densities. - Plots of densities at various temperatures for the nitric acid and water system from 50- to 100-percent nitric acid are shown by figure 9(a). This plot is based principally on data from reference 19. The data for the more concentrated acids are extrapolated to higher temperatures with the aid of data supplied by the General Chemical Division, Allied Chemical and Dye Corporation for 97.5-percent $HNO_3$. The data for temperatures below $0^\circ$ C are extrapolated linearly.

Densities of the nitric acid and nitrogen tetroxide system at several temperatures are reported in references 19, 25, and 28. Reference 28 also reports some densities of the nitric acid, nitrogen tetroxide, and water system (fig. 9(b)).

Densities at several temperatures within the range $3^\circ$ to $35^\circ$ C for the ternary system nitric acid, sulfuric acid, and water are reported in reference 33. A plot of constant-density lines at $15^\circ$ C on a ternary diagram (reference 33) is shown by figure 9(c).

Viscosities. - Viscosities at various temperatures for the binary system nitric acid and water are reported in references 24 and 34 to 36. The data of references 34 to 36 agree fairly well at the higher temperatures; but at lower temperatures, the data of reference 36 are more erratic for 50- to 100-percent nitric acids. The viscosities reported in reference 24 are much lower. The data of reference 34 for 50- to 100-percent nitric acids are shown plotted in figure 10, the dashed curves representing extrapolations from a linear plot made on an A.S.T.M. standard viscosity-temperature chart. Similar plots of the data of reference 35 are also linear on A.S.T.M. charts at $0^\circ$ to $75^\circ$ C and the extrapolated data are generally similar to those shown in figure 10. For the more concentrated acids, however, the viscosities of reference 35 are somewhat lower than those shown in figure 10. The viscosities of all observers (references 24 and 34 to 36) show maximums occurring at various temperatures in the region of approximately 60 to 70 percent nitric acid.

Viscosities of the ternary system nitric acid, sulfuric acid, and water are reported in references 34 and 35, and the ternary plots published therein show generally similar trends. The data of reference 35 cover a wider temperature range and, allegedly, the viscosity trends for the ternary system are better defined because of more determinations.

Constant-viscosity lines at 0°, 25°, 50°, and 75° C for the system 50 to 100 percent nitric acid, 0 to 50 percent sulfuric acid, and 0 to 50 percent water (reference 35) are shown by figure 11.

Thermodynamic properties. - A study of the thermodynamic properties of nitric acid and its mono- and trihydrates is reported in reference 22. Some of these data are included in the following table:

| | $HNO_3$ | $HNO_3 \cdot H_2O$ | $HNO_3 \cdot 3H_2O$ |
|---|---|---|---|
| Enthalpy of formation of liquid at 25° C, cal/mole | -41,349 | ----- | ----- |
| Enthalpy of vaporization at 25° C, cal/mole | 9355 | ----- | ----- |
| Enthalpy of fusion, cal/mole | 2503 | 4184 | 6954 |
| Enthalpy of infinite dilution, cal/mole | -7971 | -4732 | -2123 |
| Entropy of liquid, cal/(°C)(mole) | 37.19 | 51.84 | 82.93 |

The specific heats of these substances are shown in figure 12 plotted as functions of temperature.

Other data reported in reference 22 are free-energy functions of liquid and gaseous nitric acid, entropies of gaseous nitric acid, and free-energy functions and equilibrium constants for the following reactions at 275° to 500° K:

$$3NO_2 + H_2O(g) \longrightarrow NO + 2HNO_3(g), \quad \Delta H_o^o = -7203 \text{ cal} \tag{7}$$

$$H_2O(g) + 2NO_2 + \frac{1}{2} O_2 \longrightarrow 2HNO_3(g), \quad \Delta H_o^o = -19{,}998 \text{ cal} \tag{8}$$

$$H_2O(g) + \frac{3}{2} O_2 + 2NO \longrightarrow 2HNO_3(g), \quad \Delta H_o^o = -45{,}588 \text{ cal} \tag{9}$$

Heat-transfer properties. - Thermal conductivities for 99-percent nitric acid from -30° to 120° F have been determined under sponsorship of the NACA at the Engineering Experiment Station, Purdue University, and are shown by figure 13. The data are extrapolated above 120° F.

The boiling-film transfer coefficient for 98- to 99-percent nitric acid at 20 millimeters of mercury is reported to be about 125 Btu per square foot per hour per $^{o}F$ for a surface-to-bulk temperature difference of $25^{o}$ to $41^{o}$ F (reference 37).

Electrical conductivities. - A ternary diagram of specific electric conductances at $0^{o}$ C for the system nitric acid (80-100 percent), nitrogen tetroxide (0-20 percent), and water (0-20 percent) is shown by figure 14 (reference 38). The values of specific conductance for the binary system nitric acid and water at $0^{o}$ C are in close agreement with those of reference 11. In reference 36, specific conductances for the same binary system are somewhat lower than those of references 11 for the temperatures $0^{o}$ and $30^{o}$ C.

General comments. - Although a considerable amount of useful information on the physical properties of various nitric acids does exist, data are often fragmentary in the temperature and concentration ranges of interest to the rocket industry. Data that are especially needed are thermal-conductivity values for most of the nitric acid oxidants used in rockets, and freezing points, densities, vapor pressures, vapor compositions, and viscosities for the system nitric acid, nitrogen tetroxide, and water. The experimental determination of physical properties at high temperatures is complicated by the thermal decomposition of the acid and this factor should be taken into account in the evaluation of published data.

The data compiled for anhydrous and white fuming nitric acids are probably adequate for most engineering applications although verification of some of the extrapolated data would be desirable.

Considerable data have been reported for the system nitric acid, sulfuric acid, and water, most of which are compiled in reference 21. Although extension of the data over a wider temperature range would be helpful, the existing data are of considerable value to a rocket engineer.

## Corrosion

The value of experimental corrosion data is dependent upon the length of the testing period, especially at ambient temperatures when corrosion rates are usually small (reference 39). Under such conditions, the data are significant only for the period of testing and cannot be extrapolated safely to much longer periods; consequently, extensive field testing is required for accurate evaluation of long-term corrosion resistance of materials. When corrosion rates are high, as at high temperatures for example, short-period laboratory testing may be more reliable since experimental and field conditions are more nearly

alike; that is, the testing period approaches the expected life in service. Other factors that can influence the reliability of corrosion data are heat treatment of the sample, welding and subsequent heat treatment, condition of the surface of the material, purity of the acid, and geometry of the sample. Measured rates of corrosion are of little significance unless corrosion is of an over-all nature. Pitting and intergranular attack can seriously impair the usefulness of containing equipment even though relatively little metal is removed in the processes.

The effects of structure and composition on the corrosion of austenitic stainless steels are reviewed in references 40 to 42. Resistance of these steels to corrosion is attributed to their passivity, the theory of which is discussed in reference 43. Intergranular corrosion is apparently promoted by chromium carbide migrating to the grain boundaries. The function of titanium and niobium (columbium) added to stainless steels is to form stable carbides, thereby reducing the tendency of chromium to form its carbide; thus, AISI type 347 stainless steel, containing niobium, is one of the most corrosion-resistant of all stainless steels. Metallurgical studies of type 347 steel (references 44 to 46) indicate that heat treatment which promotes chromium carbide precipitation increases the corrosion rate in nitric acid as shown in table I (reference 47). Extra-low-carbon type 347 steel is more resistant to corrosion and the rate is little affected by heat treatment because there is less tendency to form carbides in this alloy.

The corrosion rates listed in table I were obtained in boiling 65-percent nitric acid, but the behavior of metals in such dilute acid is not necessarily indicative of their behavior in concentrated acid. For comparative purposes, however, the tests are probably satisfactory.

The effects of the atmosphere in which heat treatment is performed have been studied (references 44 and 45) but are still not understood completely.

The addition of hydrated aluminum nitrate to both red and white fuming acids to suppress corrosion has been studied (references 45, 47, 48, and 49). As shown in table II (reference 45), the addition of 1 percent hydrated aluminum nitrate appreciably decreases the corrosion rate of type 347 stainless steel. Subsequent tests, shown in table III (reference 47), indicate that the addition of water, equivalent to that contained in the hydrate, is equally effective.

Other inhibitors tested include sulfuric acid, phosphoric acid, potassium dichromate, boric acid, and potassium nitrate (references 50 and 51). Figure 15 shows the effects of the addition of sulfuric and phosphoric acids on the corrosion rate of mild steel in red fuming nitric acid at ambient temperature (reference 51). With sulfuric acid, there is a rapid decrease in rate. With phosphoric acid, the corrosion

rate passes through a minimum at approximately 1-percent addition. Beyond this point, further addition causes a substantial increase in the corrosion rate. The addition of these acids causes the formation of precipitates in the nitric acid, presumably nitrosyl sulfuric acid and nitrosyl phosphoric acid, respectively. Potassium nitrate is of interest because of its use as a flame suppressor, but it is not as effective as the other agents in reducing corrosion rate. Potassium dichromate and boric acid are approximately as effective as potassium nitrate. Aluminum is affected much more adversely by the presence of impurities in the acid, such as sulfuric acid, sulfates, chlorides, and salts of heavy metals (references 39, 51, and 52). Experimental corrosion rates are given in references 39, 43, 46 to 48, 50, 51, and 53 to 56 for stainless steels, aluminum alloys, and other metals.

A comparison of aluminum and stainless steels shows that if the nitric acid concentration is greater than about 90 percent, the corrosion resistance of aluminum is slightly superior to the resistance of stainless steels (references 53, 57, 58). Below 90 percent, the corrosion rate for aluminum increases sharply and stainless steels are superior. Figure 16 shows the effect of acid concentration at ambient temperatures on the corrosion rates of 99.3-percent aluminum and 2S-H aluminum (references 57 and 58). Stainless steels and aluminum alloys both show a sharp increase in corrosion rates with increasing temperature. Figure 17 shows the effect of temperature on types 304 and 347 stainless steels in both red and white fuming nitric acids (references 39 and 48).

Data also show that the vapor phase above concentrated nitric acid is more corrosive to aluminum than is the liquid phase (reference 39), while the reverse is true for stainless steels. Presumably, the presence of moisture forms a dilute acid which is highly corrosive to aluminum. Figure 18(a) compares the corrosion rates at ambient temperature of several aluminum alloys exposed (1) simultaneously to both the liquid and vapor phases of 6.5-percent red fuming nitric acid and (2) only to the liquid phase (reference 39). Figure 18(b) shows a similar comparison for several stainless steels (reference 39).

Aluminum alloys are definitely superior to stainless steels for long-term exposure to fuming nitric acids at ambient temperature. Corrosion rates for these alloys remain fairly constant with time while those for stainless steels increase (reference 39). Aluminum is slightly superior to its alloys and its corrosion resistance increases with purity of the metal (reference 59). At higher temperatures, aluminum alloys are susceptible to pitting; the 2S alloy is best in resistance to this type of attack (reference 51). The corrosion resistance of aluminum alloys is also practically independent of heat treatment, whereas, as previously indicated, stainless steels are extremely sensitive to the type of heat treatment (references 47 and 48).

In general, red fuming nitric acid appears to be more corrosive than white fuming nitric acid. In mixed acid, type 347 stainless steel is decidedly superior to the aluminum alloys as shown in figure 18(c)(reference 56). Mixed acid is more corrosive than red fuming nitric acid with aluminum alloys, whereas the opposite is true with stainless steels.

Titanium has a corrosion rate of less than 1 mil per year in various concentrated acids, including red fuming nitric acid (references 48 and 60 to 62). Zirconium gains weight slightly when exposed to nitric acid (references 48 and 60 to 62); however, it is highly resistant to corrosion. Tantalum (reference 61) and tantalum-molybdenum alloys containing over 40 percent tantalum (reference 63) show absolutely no attack by 70-percent nitric acid. Teflon, a fluorinated hydrocarbon, is inert to nitric acid (references 53 and 56).

Summary. - On the basis of rather complete laboratory and field tests, 2S and 3S aluminum alloys have the greatest corrosion resistance to fuming nitric acids among the commonly available materials, whereas stainless steels are more corrosion-resistant to mixed acids. Of the stainless steels, AISI type 347 and 304 have the greatest corrosion resistance to fuming nitric and mixed acids.

The results of preliminary or incomplete tests can be summarized as follows:

(1) The addition of water to fuming nitric acids suppresses the corrosion rates of stainless steel, even when the water is combined as in hydrated aluminum nitrate.

(2) Small additions of sulfuric or phosphoric acids to fuming nitric acids decrease their corrosiveness.

(3) Titanium, zirconium, tantalum, and tantalum-molybdenum alloys are all very resistant to attack by concentrated nitric acids.

(4) Of the nonmetallic materials, highly fluorinated hydrocarbons, such as Teflon, are inert to nitric acid.

## Thermal Stability

Nitric acid of high concentration dissociates spontaneously even in the dark according to the following equation (reference 64):

$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O \qquad (10)$$

The anhydride dissociates by some mechanism causing more acid to decompose to maintain the equilibrium. At a certain dilution, the excess of water practically stops the reaction (reference 65).

The rate-controlling step in nitric acid decomposition involves the decomposition of the nitrogen pentoxide according to one of the following equations:

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2 \qquad \text{(reference 65)} \qquad (11)$$

$$N_2O_5 \longrightarrow N_2O_3 + O_2 \qquad \text{(references 66 and 67)} \qquad (12)$$

$$N_2O_5 \longrightarrow NO_3 + NO_2 \qquad \text{(reference 68)} \qquad (13)$$

Although the dissociation of $N_2O_5$ has been studied extensively under a variety of conditions (references 66 to 77), the exact mechanism is still in doubt; it appears, however, that either reaction (12) or reaction (13) represents the rate-determining step. In any event, further reaction leads to the following over-all decomposition reaction:

$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \frac{1}{2} O_2 \qquad (14)$$

Above 63-percent nitric acid concentration, the solubility of oxygen in the acid decreases rapidly with increasing acid concentration and is almost zero at 79-percent concentration (reference 78). It is this insolubility of oxygen in the acid which causes a pressure build-up in enclosed containers even though only a relatively small amount of oxygen is formed. The resulting high pressures will also influence pump design in that exceedingly high suppression pressures will be required to prevent cavitation and vapor lock.

Nitrogen dioxide is about as soluble in absolute nitric acid as ammonia is in water. The following assumed equilibrium is very sensitive to temperature changes (reference 28):

$$HNO_3 \cdot NO_2 + H_2O \rightleftharpoons HNO_3 \cdot H_2O + NO_2 \qquad (15)$$

Nitric acid decomposition also has been studied in the gas phase (reference 79). From about 100° to 400° C, the reaction as represented by equation (14) is heterogeneous and initially first order with a low critical increment of about 5 kilocalories. The rate is reduced by the presence of water or nitrogen dioxide. Above 400° C, the reaction is

homogeneous and first order with the products having no effect on the reaction rate. Decomposition of nitric acid at ambient temperatures, however, does not appear to be associated with gas phase reaction types, but with homogeneous liquid phase decomposition (reference 80).

With available thermodynamic data and some basic assumptions, the theoretical effect on decomposition of variables such as the initial composition of the acid and the gas-phase volume in an enclosed container has been determined in a qualitative manner (reference 81). Figure 19 shows theoretical relative equilibrium pressures obtained for various amounts of water and nitrogen dioxide in nitric acid. From these curves, it can be seen that water is more effective than nitrogen dioxide in reducing equilibrium pressures above about 95-percent acid concentration and also that a combination of the two is the most effective. The curve for the ternary system is based on a nitrogen dioxide - water molal ratio of 4. Other theoretical considerations corroborate the lowering of equilibrium pressure by nitrogen dioxide and water and, in addition, indicate that the addition of nitrate ions should also reduce the pressure (reference 80).

Figure 20 shows the rate of pressure rise for acids with various compositions and with various ullages (reference 82). These data were obtained in glass apparatus. Table IV shows similar data as well as the pressures recorded after an interval of several hours (reference 80). In figure 20, it can be seen that (1) the smaller ullages give rise to higher pressures, (2) acid containing appreciable amounts of nitrogen dioxide (curve 3) approaches an equilibrium pressure faster than does the anhydrous acid or white fuming nitric acid, and (3) this pressure is lower than that obtained with the other acids.

Similar data are reported in reference 83, and figure 21 shows equilibrium pressures as a function of temperature. Figure 22 shows the time required for white fuming acid to reach equilibrium as a function of temperature (reference 83). The attainment of equilibrium with red fuming acid was too rapid to be measured with the same apparatus. Apparently, the time to reach equilibrium is a function of experimental conditions, since an appreciable length of time was required for red fuming acid to reach equilibrium in reference 82 (fig. 20).

For red fuming nitric acid in glass apparatus, figure 23(a) (reference 84) gives bubble point pressures as a function of temperature. For white fuming acid in glass apparatus, figure 23(b) (reference 85) gives bubble point pressures as a linear function of time.

Actual proof of an equilibrium has been established as shown in figure 24 (reference 82). After an equilibrium pressure was reached at 122° F, the temperature was increased to 160° F; when the temperature was decreased to 122° F, the same equilibrium pressure was attained. The existence of such an equilibrium is also substantiated in reference 86.

Figure 25 shows decomposition pressures obtained with both red and white fuming nitric acids in type 347 stainless steel apparatus (reference 87). In each case, the pressure passes through a maximum and then decreases apparently to an equilibrium pressure. With red fuming acid, the maximum pressure is considerably less and is reached slightly faster than with white fuming acid. The pressure decreases may have been due to leaks in the system; however, the same phenomenon has been described in cases where leaks were probably not present (reference 80). In the case of metals, an explanation may be found in a postulate of two competing reactions (reference 80): (1) the decomposition reaction and (2) the corrosion reaction. The latter does not begin until the end of an induction period and at that time it proceeds more rapidly than the concurrent decomposition reaction. The corrosion reaction uses up the oxygen produced by the decomposition reaction and thus reduces the pressure.

In other instances, storage data on white fuming acid in 3S aluminum tanks show that a pressure of 50 pounds per square inch gage developed in 24 hours at 122° F and in less than two weeks at temperatures averaging 80° F. A maximum pressure of 80 pounds per square inch gage was recorded for red fuming acid in stainless steel and aluminum drums for a 7-month period. The maximum temperature during the period was 111° F (reference 87).

Prolonged storage of acids in metal containers results in weakened acids, the extent of deterioration depending on the temperature and the length of storage time. The reduction of acid concentration is due to the corrosion reaction or the decomposition reaction or more probably a combination of the two. Examples of how storage affects acid composition are given in the following table for red fuming acid stored at 120° F for 5 months (reference 87):

| Red fuming nitric acid (stored at 120° F) | Composition, weight percent | | |
|---|---|---|---|
| | Original | After 5 months in type 347 stainless steel container | After 5 months in 3S aluminum container |
| $HNO_3$ | 91.36 | 80.26 | 87.79 |
| $NO_2$ | 7.04 | 10.42 | 10.27 |
| $H_2O$ + metal nitrates | 1.60 | 9.32 | 1.94 |

Summary. - Problems connected with the use of concentrated nitric and mixed acids, especially at high temperatures, include the following: (1) development of high pressures in storage, (2) cavitation and vapor lock at pump inlets, (3) corrosion of containers, (4) acid deterioration, and (5) sludge formation. Usage requirements will determine the most serious of these problems. For example, high pressures may not be a problem in a pressurized propellant feed system, while in a storage drum these high pressures might be serious. Methods have been developed for at least partial control of each of these problems but usually at the expense of some desirable property. For example, addition of nitrogen dioxide to nitric acid decreases both the melting point and the thermal decomposition pressure. The vapor pressure, however, is increased; the tendency towards cavitation and vapor lock in a turbine-driven pump is thereby increased and sturdier containers are required. As another example, the addition of ammonium nitrate to white fuming acid lowers the melting point and decreases the thermal decomposition pressure slightly. In this case, however, the ignition properties are seriously impaired. It appears, therefore, that a considerable amount of work on these problems is desirable in order that more satisfactory solutions can be obtained.

## CONSTITUTION AND ANALYSIS

### Constitution

A knowledge of the exact constitutions of nitric acids of various compositions is important in elucidating the mechanisms of reactions involving these substances. Cryoscopic and Raman spectroscopic techniques have been very useful in securing this knowledge. By these means, it has been shown that anhydrous nitric acid dissociates spontaneously into ionic and molecular species and that, in aqueous solutions, the constitution changes markedly with changes in concentration. Components of mixtures of nitric acid with nitrogen oxides and with sulfuric acid have also been identified by these methods.

Spontaneous dissociation of anhydrous nitric acid. - In addition to molecular nitric acid, the Raman spectrum of absolute nitric acid always shows the presence of the nitronium ion $NO_2^+$ (reference 88) and the nitrate ion $NO_3^-$ (reference 89). These two ions, along with water, constitute the products of the self-ionization of nitric acid that proceeds according to the following equation (reference 89):

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (16)$$

This equation neglects the solvation of the products by nitric acid. Cryoscopic measurements in nitric acid have also shown this dissociation (reference 90) and have further indicated that each of the products is solvated with two molecules of nitric acid.

It has been estimated from spectroscopic measurements that anhydrous nitric acid contains 1.0 ± 0.2 percent nitronium ions by weight and 1.5 ± 0.3 percent nitrate ions by weight (reference 89). Assuming that equation (16) is accurate and taking into account an estimated 0.4 percent by weight of water that is probably present as a nitric acid hydrate, it was calculated that about 3 percent by weight of anhydrous nitric acid is self-dissociated. Although not indicated directly, the temperature at which these experiments were conducted and at which these data are applicable was probably -15° C (references 88 and 90).

Cryoscopic measurements in nitric acid at -40° C are in general agreement with these deductions (reference 90). It was further concluded from these measurements that another 10 percent of the nitric acid is bound in solvates of the dissociation products.

The reversal of the equilibrium represented by equation (16) was demonstrated in part when it was found that the addition of about 1.5 percent of water by weight to anhydrous nitric acid is sufficient to reduce the nitronium ion concentration to an unmeasurable degree (reference 91). At the same time, the nitrate ion concentration also decreases (reference 15). Further confirmations of this equilibrium are presented in reference 89.

Autoprotolysis resulting in nitric acidium and nitrate ions has been suggested as another possible mode of self-dissociation of nitric acid (reference 89):

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \qquad (17)$$

Although this reaction cannot be the principal mode of self-dissociation because the nitronium and nitrate ions are found to be approximately equivalent, there is a possibility that 10 to 15 percent of the total dissociation may consist of this autoprotolysis (references 15 and 90).

Mixtures of nitric acid and water. - As water is progressively added to nitric acid, the concentration of nitrate ions passes through a minimum, since the water destroys them by equilibrium (16) and produces them by the following equilibrium:

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^- \qquad (18)$$

The nitrate ion concentration remains very small until about 10 percent by weight of water has been added (references 91 to 93). Corroboratively, the conductivity of nitric acid containing as much as 10 percent water is not much greater than that of anhydrous nitric acid (references 11 and 94). Even in solutions containing 22 percent water (equimolecular mixtures of nitric acid and water), the ionization as shown by equation (18) is not more than 2 percent.

Although water forms very few ions, it does form stable solvates with nitric acid (references 90, 95, 96, 97), but the compositions are not known definitely. In solutions containing 0 to 5 percent water, cryoscopic measurements indicate that the complex is $H_2O \cdot 2HNO_3$ (reference 90). Vapor pressure studies indicate that, in solutions containing 5 to 20 percent water by weight, the monosolvate $H_2O \cdot HNO_3$ is produced (reference 97). The disolvate may be formed in the more concentrated solutions because many nitric acid molecules are competing for each water molecule.

Mixtures of nitric acid and nitrogen tetroxide. - From a kinetic study of the effect of nitrogen tetroxide on nitration in certain mediums, it has been suggested that this oxide ionizes in nitric acid to produce nitrosonium and nitrate ions as follows (reference 15):

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \tag{19}$$

This ionization may be repressed by the addition of alkali nitrates (reference 98). The equation also expresses the self-dissociation of pure liquid nitrogen tetroxide (reference 99). In dilute solutions, nitrous acid exists in nitric acid largely as nitrogen tetroxide, but an increase in the concentration of nitrogen tetroxide or water increases the small proportion in which it exists as nitrogen trioxide (reference 15). The equilibrium is shown by the following equation:

$$2N_2O_4 + H_2O \rightleftharpoons N_2O_3 + 2HNO_3 \tag{20}$$

Nitrogen trioxide ionizes in nitric acid in a manner similar to that of nitrogen tetroxide (reference 15):

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^- \tag{21}$$

The suggested ionization of $N_2O_4$ in dilute solutions in nitric acid has been confirmed by Raman spectroscopic evidence that also showed no formation of nitronium or nitrite ions (reference 98). The spectrum of the nitrogen tetroxide molecule was completely absent, leading to the conclusion that the concentration of nonionized $N_2O_4$ in these solutions is very small. Since these experiments were conducted with the solutions maintained at 20° C, it is possible that spectroscopically observable quantities of molecular $N_2O_4$ may be present at lower temperatures. Since nitrate ions are formed by equation (19) as well as by the self-dissociation of nitric acid represented by equation (16), a mass-law repression of the latter upon the addition of $N_2O_4$ decreases the nitronium ion concentration as the nitrate ion concentration increases.

A small amount of nonionized nitrogen dioxide was also found in the solutions. Its presence was indicated spectroscopically as well as by the yellow color of the solutions. The practically complete dissociation of $N_2O_4$ molecules in dilute solution (up to at least 10 percent $N_2O_4$ by weight) in nitric acid partly into $NO_2$ molecules but mostly into nitrosonium nitrate may be represented in total by the following equilibriums (reference 98):

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^- \tag{22}$$

Had the solutions been examined spectroscopically at lower temperatures (for example, 0° C), the Raman lines of the $NO_2$ molecules might have been found to be absent and, as mentioned previously, the $N_2O_4$ molecule might have been detected because of the thermally shifting equilibrium that exists between the monomeric and dimeric forms (reference 100):

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{23}$$

Pure colorless solid $N_2O_4$ liquifies on heating and is converted slowly to $NO_2$ as the temperature is raised. At 22° C, the reddish-brown equilibrium mixture is about 20 percent $NO_2$ and 80 percent $N_2O_4$ by weight. At 140° C, the resultant black gas is mostly $NO_2$.

As a solvent for nitrogen tetroxide, nitric acid exhibits a character intermediate between that of sulfuric acid and nonpolar organic compounds. As shown cryoscopically and spectroscopically, $N_2O_4$ dissociation in sulfuric acid is entirely heterolytic (references 101 and 102) (see equation (22)). The fission in nonpolar solvents is wholly homolytic (equation (22)). As discussed previously, both types of dissociation are observed in nitric acid.

Mixtures of nitric acid and sulfuric acid. - Cryoscopic measurements of solutions of nitric and sulfuric acids ("mixed acids") offer proof that the two acids react to form nitronium, hydronium, and hydrogen sulfate ions as follows (reference 101):

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (24)$$

The conversion of nitric acid is practically complete in dilute solutions of nitric acid in sulfuric acid (for example, 10 percent $HNO_3$ and 90 percent $H_2SO_4$). Similarly, in dilute solutions of sulfuric acid in nitric acid (for example, 10 percent $H_2SO_4$ and 90 percent $HNO_3$), the conversion of sulfuric acid is practically complete. Mixtures of intermediate composition retain various amounts of molecular nitric and sulfuric acids (reference 88). Since water is not ionized completely in sulfuric acid, the pertinent product ions in equation (24) reunite partially as in the left direction of the following equilibrium (reference 103):

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad (25)$$

The ionization of equation (24) can be reversed by the addition of water or an acid salt of sulfuric acid such as potassium hydrogen sulfate (reference 88).

As shown by a study of freezing points, other molecular species often found in nitric acid solutions react similarly in sulfuric acid (reference 101):

$$N_2O_5 + 3H_2SO_4 \longrightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^- \qquad (26)$$

$$N_2O_4 + 3H_2SO_4 \longrightarrow NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^- \qquad (27)$$

$$N_2O_3 + 3H_2SO_4 \longrightarrow 2NO^+ + H_3O^+ + 3HSO_4^- \qquad (28)$$

Raman spectra of solutions of various nitrogen oxides in sulfuric acid offer additional evidence of the ionization reactions shown by these equations (reference 102).

Nitrogen pentoxide. - Solid nitrogen pentoxide does not exist in the molecular form but in some modified configuration (reference 104) now interpreted as the ionic species $(NO_2^+)$ $(NO_3^-)$ (references 105 to 107). When nitrogen pentoxide is dissolved in nitric acid, the ions

merely disperse in the solution. Any solution, therefore, that contains nitronium and nitrate ions regardless of the original source may be considered as containing nitrogen pentoxide. Raman spectra of solutions of $N_2O_5$ in nitric acid show no evidence of covalent molecular nitrogen pentoxide. It can and does exist, however, in neutral solvents such as carbon tetrachloride, chloroform, or phosphorus oxychloride (references 104, 108, and 109). In the vapor phase, the anhydride consists of $N_2O_5$ molecules.

Summary. - The constitutions of nitric acid and some of its solutions are summarized as follows:

1. Anhydrous nitric acid undergoes self-dissociation to the extent of approximately 3 percent by weight according to the following equation:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (16)$$

2. Addition of water to anhydrous nitric acid suppresses the self-dissociation. In solutions containing up to 5 percent water, the disolvate $H_2O \cdot 2HNO_3$ is produced; in solutions containing 5 to 20 percent water, the monosolvate $H_2O \cdot HNO_3$ is formed. Ionization is small in solutions up to about 20 percent water. Addition of more water increases the ionization.

3. Nitrogen tetroxide dissociates in nitric acid according to the following equation:

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (19)$$

Solution of nitrogen tetroxide in nitric acid inhibits self-dissociation of the latter by increasing the total nitrate ion concentration.

4. In mixtures of nitric and sulfuric acids (mixed acids), ionization occurs by the following mechanism:

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (24)$$

5. Since solid nitrogen pentoxide is actually completely ionized nitronium nitrate, its dissolution in nitric acid is merely a dispersion of the ions in the solution.

## Analysis

The analysis of nitric acid is of importance to both research and operations engineers because relatively small changes in water content can profoundly affect the ignition characteristics of this oxidant and because metallic contamination from storage containers can lead to objectionable deposits in a rocket engine. Analysis is also useful in estimating the degree of thermal decomposition of the acid.

For fuming nitric acids, the principal determinations are total acidity, oxides of nitrogen as nitrogen dioxide, water, and metallic salt content. In mixed acids, sulfuric and "nitrosylsulfuric acid" contents are also determined.

Anhydrous, white fuming, and red fuming nitric acids. - A novel method of concentrated nitric acid analysis (85 to 100 percent) utilizes the straight-line relation between nitric acid concentration and surface tension (reference 110). The presence of nitrogen oxides up to 6 percent does not affect the results. It is claimed further that the nitric acid and nitrogen dioxide contents of the acid can be determined in a few minutes with an accuracy of 0.3 to 0.4 percent by simultaneous measurements of density and surface tension.

The classical volumetric method for analyzing uncontaminated nitric acids (reference 111) has often been modified by various analysts to suit their particular requirements (for example, reference 112); however, the different methods are still essentially the same.

Total acidity: Determination of total acidity (sum of all acidic constituents) is made by direct titration with an aqueous solution of sodium hydroxide. Sometimes, excess caustic is used and back-titration is accomplished with hydrochloric acid (references 112 to 116).

Oxides of nitrogen: Oxides of nitrogen are usually determined as nitrogen dioxide by oxidation with ceric sulfate and back-titration with ferrous sulfate using ferroin as an indicator (references 116 and 117). Weight percent nitrogen dioxide as nitric acid is subtracted from total acidity to obtain the actual amount of nitric acid present.

Water: Water content is taken as the difference between 100 percent and the sum of nitrogen dioxide and nitric acid. Since this involves a small difference between large numbers, small percentage errors in the large numbers lead to large percentage errors in the water content. This procedure constitutes the primary weakness of the classical analysis and a direct determination of water content would be more desirable.

Several direct methods for the analysis of water in nitric acid are now being developed. These include an infrared absorption technique, titration with Karl Fischer reagent, and measurement of electrolytic conductivity.

In the first method, the water assay is obtained by absorption of near-infrared radiation at about 1.43 microns (references 118 and 119). It has been concluded that this determination is independent of nitrogen dioxide or dissolved metal (Fe, Ni, Cr, Al) salt content. The equipment required is quite expensive and not generally available, but the method appears to be promising where large numbers of routine analyses are required.

Titration with Karl Fischer reagent is another promising method that requires only simple equipment available in most analytical laboratories (reference 120). Nitrogen dioxide, at least to 1.5 percent, and normal amounts of dissolved metallic salts do not interfere significantly with the determinations (reference 120). Correction factors to account for any interference by nitrogen dioxide at least to 15 percent by weight have been proposed (reference 121).

A third proposed method for water determination involves measurement of electrolytic conductivities (reference 122). Since nitrogen dioxide interferes with the determination, a satisfactory solution of the problem is envisioned in the simultaneous determination of both water and $NO_2$ contents. The analytical procedure will probably entail a minimum of three conductivity measurements necessary to produce two ratios from which the two unknowns can be determined. At present, the effect of dissolved metallic salts is not known.

Until more experience is accumulated with each of these three direct methods for assaying water, it will be difficult to establish which method is most suitable for routine laboratory determinations.

Mixed acids. - Mixed acids, mixtures of nitric and sulfuric acids, are analyzed by methods similar to those used with other nitric acids (reference 123).

Total sulfuric acid content is obtained by caustic titration after the nitric acid has been evaporated from the weighed sample. Nitrosyl - sulfuric acid ($NOHSO_4$) is determined by the ceric sulfate - ferrous sulfate method used for nitrogen dioxide in fuming nitric acid. Water is determined by difference.

Metal-contaminated acids. - Although little information exists in the literature on methods of analysis for nitric acids containing metal contaminants, a few fairly satisfactory means for correcting total acidity for their presence have been described recently (reference 112).

In one method (reference 124), excess caustic is added to an acid sample containing iron as an additional component. The resultant precipitate is filtered off and the filtrate back-titrated with hydrochloric acid. The titration is then corrected for the contaminant. A similar method for iron-, chromium-, and nickel-contaminated acid is reported in reference 125. Both methods result in some inaccuracy in water content calculated as a difference. A more refined procedure that yields total acidity of greater accuracy has been described (reference 126).

The metallic contaminants are usually determined by spectrophotometric methods and other standard analytical procedures (for example, references 120 and 127).

General comments. - Many molecular and ionic species that are actually present in concentrated nitric acid solutions and that have been discussed previously cannot be determined by the ordinary methods of analysis outlined herein. A knowledge of the quantitative content of the various species comprising nitric acid may become increasingly important as their individual effects in practical applications, such as rocket engine performance, become known. Modifications of Raman spectrographic technique or some other unexploited method may provide the desired means of obtaining this information.

## REACTIONS IN A ROCKET ENGINE

Among the many classes of fuels considered for use with nitric acid in rocket engines have been alcohols (reference 128), ammonia derivatives (reference 129), mercaptans (reference 130), and hydrocarbons (references 131 and 132). Some specific fuels considered in these broad classifications are: furfuryl alcohol, ammonia, hydrazine, various amines, "mixed butyl mercaptans", dienes, acetylenic compounds, turpentine, gasoline, and jet fuels.

The suitability of specific fuels is generally ascertained through ignition-delay studies (reference 133), specific-impulse analyses, and empirical studies. Scant attention has been given to the mechanisms of the chemical processes that take place prior to and during combustion of the fuel-oxidant mixture. In this section, types of reactions which could occur in a rocket engine are discussed with emphasis on reactions of nitric acid oxidants.

### General Considerations

In order that self-ignition and combustion take place in a rocket engine, heat must be evolved very rapidly upon the mixing of fuel and oxidizing agent. This implies that, of all the possible physical and

chemical reactions that may take place, there must be some that liberate heat in such large quantities and so rapidly that the effect of all those reactions that would absorb heat is effectively masked.

Although each fuel is capable of a great variety of reactions because of its individual chemical nature, it appears possible to select a few general reaction types that all fuels currently considered for use with a nitric acid type oxidizing agent seem capable of undergoing. Thus, as a last stage in the various processes taking place in the rocket engine, the fuel must be oxidized to such an extent that its molecular structure is destroyed and simple molecules like carbon dioxide, carbon monoxide, water, and nitrogen are formed. Most of the energy evolved from the combustion finds its source in this destructive oxidation.

The types of reactions which could take place under rocket engine conditions are acid-base reactions, nitration, and oxidation. The physical reactions of mixing and solution are probably of minor importance as sources of heat energy.

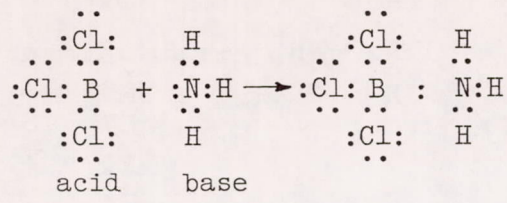
In some cases, synergistic effects are observed in the ignition process. For example, two fuels, each of which has mediocre ignition characteristics with nitric acid, may have very desirable ignition properties when mixed in proper proportions. A number of explanations are possible for such behavior. It may be assumed, for example, that concurrent reactions are taking place. If a reaction of one fuel has a low activation energy and a low enthalpy of reaction while a reaction of the second fuel has a high energy of activation and a high enthalpy of reaction, the reaction of the first fuel may release enough energy to initiate reaction of the second fuel. The second reaction, along with the first, then supplies the energy needed to initiate combustion.

## Acid-Base Reactions

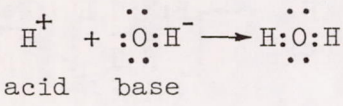
Inspection of the electronic structures of various fuels currently considered indicates that they are all capable of acting as bases toward strongly acidic reagents. Since reactions between many acids and bases either attain equilibrium very rapidly or go to completion at a high rate even at low temperatures, it would seem likely that such acid-base reactions are of particular significance in the initial stages of the ignition process. The heat evolved from these neutralizations may promote other types of reactions, such as oxidation, that are more difficult to initiate at low temperatures.

The criteria for determining whether a substance is acidic or basic under a given set of experimental conditions have been outlined in a general theory of acid-base reactions proposed by G. N. Lewis (reference 134).

According to this theory, an acid is a substance capable of accepting a share in a lone electron pair from a base to form a coordinate-covalent bond. A base, in turn, is a substance capable of donating a share in a lone electron pair to the acid. Typical examples are:

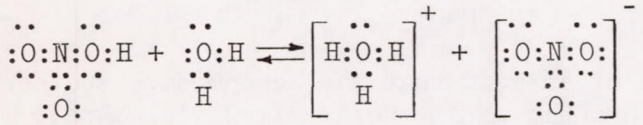



(29)




(30)

The behavior of nitric acid in various solvents is a striking example of the relative nature of acidic character. In a water medium, the familiar acid behavior of this material may be represented by:

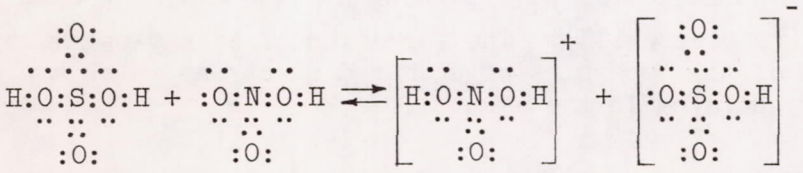


(31)

(One of several equivalent resonance forms)

(One of several equivalent resonance forms)

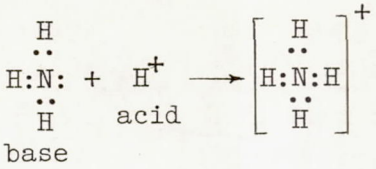
In concentrated sulfuric acid, on the other hand, nitric acid, being a weaker acid than the former, behaves as a base (reference 15).



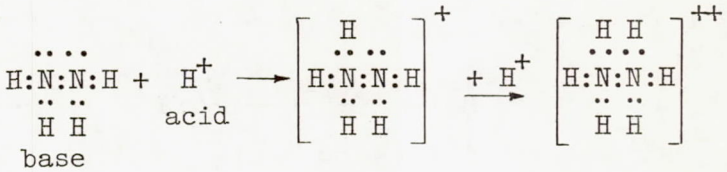
(32)

Frequently, the products of such neutralizations are reactive units (usually ions) which are capable of polymerization, of rearrangement, of spontaneous decomposition, or of some other reaction. The application of the acid-base reaction to the various classes of common rocket fuels is discussed subsequently. The various reactions of the neutralization products, however, are not discussed as such.

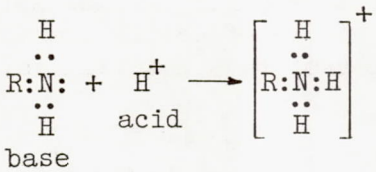
Reactions with ammonia derivatives. - The behavior of ammonia, hydrazine, and amines indicates that the nitrogen atom involved has an unshared pair of electrons. These unshared electrons lend basic character to ammonia and its derivatives.




(33)



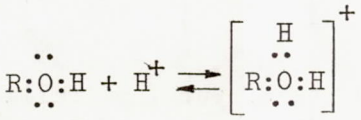

(34)




(35)

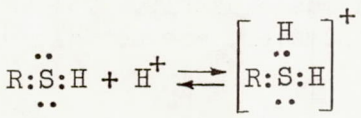
In the presence of an acid that can accommodate another electron pair in its orbits, ammonia or its derivatives will donate its unshared electrons to the setting up of a donor-acceptor bond with electron-deficient species, such as a proton derived from an oxidizing acid. This would represent an acid-base reaction in the Lewis sense. Any suitable proton source will bring about this reaction.

Reactions with alcohols, mercaptans, and related compounds. - In certain respects, alcohols behave as weak bases. They are capable of forming oxonium salts of the type $ROH_2^+ X^-$ with a strong acid like sulfuric acid (reference 135). The formation of such oxonium salts is a consequence of the two pairs of unshared electrons which are associated with the oxygen atom in the alcohol:



(36)

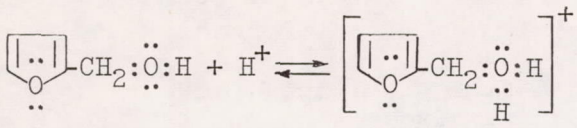
Since sulfur atoms have the same number of unshared electrons in their outer shell, they, too, may form sulfonium salts in acid medium:



(37)

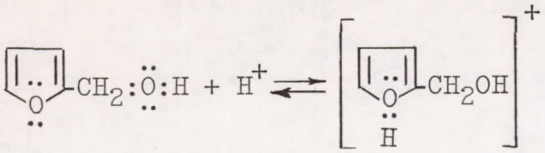
This reaction is to be expected of many organic sulfur compounds - for example, mercaptans and sulfides.

In the case of furfuryl alcohol, the primary attack of a proton may occur at one of two reactive centers, the oxygen of the hydroxyl radical or the oxygen of the ether linkage:



(38)

or

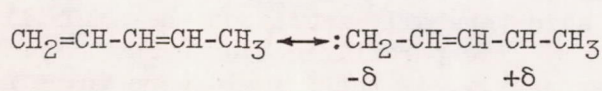


(39)

The presence of several reactive centers in a fuel may be of particular significance in rocket ignition; that is, under similar conditions, one would anticipate reaction to occur more readily if the attacking reagent had several points of attack on a fuel molecule rather than one and if other factors such as viscosity, molecular weight, and relative reactivity of the functional groups involved were comparable.

Reactions with hydrocarbons. - In the presence of acids, olefinic as well as acetylenic bonds have a tendency to polarize; that is, the electron distribution associated with a multiple bond becomes effectively such that one of the carbon atoms will appear to have a pair of electrons unshared with any other atom and the other carbon atom will be devoid of a pair of electrons. Thus, the former carbon atom will have a formal negative charge; the latter, a formal positive charge. An attacking proton from the acid can then form a new bond with the negatively charged carbon atom (reference 136). This type of reaction is quite common in the case of additions to the double bond (reference 137).

The polarization of conjugated dienes such as 1,3-pentadiene occurs readily:



(40)

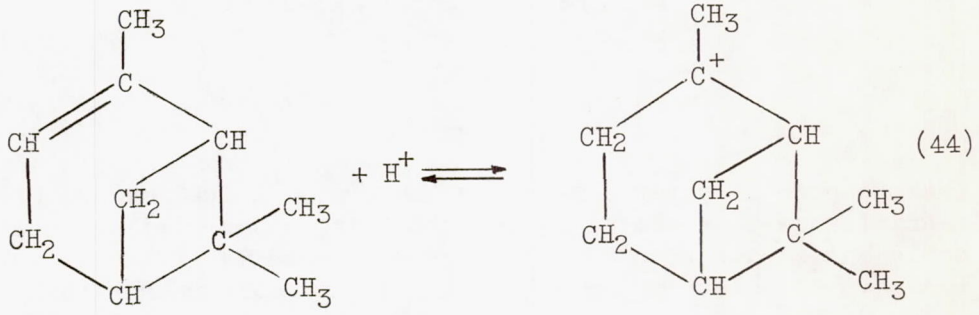
$$:CH_2\text{-}CH{=}CH\text{-}CH\text{-}CH_3 + H^+ \rightleftharpoons CH_3\text{-}CH{=}CH\text{-}CH\text{-}CH_3 \quad (41)$$
$$\quad -\delta \qquad +\delta \qquad\qquad\qquad\qquad\qquad\qquad +$$

The polarization of acetylenic compounds may be represented as follows:

$$R\text{-}C \equiv CH \longleftrightarrow R\text{-}C{=}\ddot{C}H \quad (42)$$
$$\qquad\qquad +\delta \; -\delta$$

$$R\text{-}C{=}\ddot{C}H + H^+ \rightleftharpoons R\text{-}C{=}CH_2 \quad (43)$$
$$+\delta \; -\delta \qquad\qquad +$$

The case of a mixture of terpenes is somewhat more complex. With acids, α-pinene, the chief constituent of turpentine, may react as follows:




(44)

α-pinene

In the case of a mixture of α-pinene with the other constituents of turpentine, this reaction may release sufficient heat that other types of reactions may take place in the mixture.

Whether other terpene-type compounds that do not have olefinic bonds in the molecule are suitable for rocket work has not yet been ascertained. Several types may be considered; for example, the straight-chain terpenes would probably behave like ordinary paraffinic hydrocarbons toward nitric acid, while aromatic terpenes would probably behave analogously to aromatic hydrocarbons.

The extent of the solubility of proposed fuels in acid may be considered an indication of their suitability. The neutralization of a fuel by the oxidizing acid generally increases the solubility of the fuel in the oxidizing agent. The paraffinic hydrocarbons are not too soluble in nitric acid; consequently, if these fuels were to be used in the rocket engine, the only heat produced initially would be due to the mixing of

the nitric acid and the paraffinic hydrocarbons. This effect would be quite small; therefore, the ignition of such a fuel would have to be caused by other reactions of similar rapidity and exothermic character as neutralization reactions.

## Nitration Reactions

Although nitration reactions are not sufficiently rapid to be of great importance, some discussion is warranted on the basis that side reactions of this type may lead to formation of substances that can contribute to explosive ignitions under proper conditions. The extent of the following discussion on nitration is not indicative of the importance of this type of reaction in a rocket engine, but rather reflects the vast amount of literature that is available on the subject as compared with that available for the other types of reactions discussed herein.

Nitration of aliphatic compounds. - The mechanism of the nitration of paraffins is not well understood. Since these reactions generally take place at elevated temperatures that are often much above 250° C, a temperature at which nitric acid is completely dissociated, the reaction seems to involve some of the oxides of nitrogen rather than nitric acid itself.

It has been shown (reference 138) that the nitration of saturated hydrocarbons is suppressed in the presence of nitric oxide, NO, and accelerated by oxygen. This has led to the conclusion that nitrogen dioxide, $NO_2$, can represent the active species in this reaction. The observation that nitration of aliphatic compounds proceeds quite readily in the vicinity of 100° C when gaseous nitrogen dioxide is substituted for nitric acid (references 139 and 140) is in agreement with this deduction.

It is characteristic of vapor phase nitration of aliphatic compounds that complex mixtures of mononitrated products are formed (reference 141). The products consist not only of compounds in which the nitro group has been introduced at various points in the initial paraffin, but also of products resulting from rupture at various points along the paraffinic chain and nitration of the fragments.

Considering further that the rate of nitration is not materially affected by acidic catalysts such as sulfuric acid, aluminum chloride, and titanium tetrachloride (reference 138) and that the products of vapor phase nitration of ethane are similar to those obtained on treatment of free ethyl radicals with nitric acid vapor (reference 142), a free radical mechanism for the reaction seems well supported.

In a rocket engine, it is conceivable that certain free radicals may be formed particularly during the oxidation processes. These free radicals may be nitrated by the oxides of nitrogen which are undoubtedly present in the reacting mixture at elevated temperatures. It is possible that this type of nitration may then be propagated by a chain mechanism and thus contribute to the vigor of the combustion. On the other hand, this reaction is probably of little significance in ignition processes since the initial temperatures of the reactants may be too low to permit the formation of a sufficient concentration of free radicals.

Nitration of aromatic compounds. - Rocket fuels such as aniline, diethylaniline, mixed xylidines, and furfuryl alcohol have pronounced aromatic character. Nitration reactions of such compounds are of some importance, even though they are apparently not rapid enough to account for ignition of these materials. In the combustion process, nitration of aromatic nuclei is quite unlikely.

Studies of the kinetics of nitrations have shown that the rate of reaction is greatly influenced by the nature of the solvent used. A graduated series of solvents may be set up with respect to the speed at which the nitration proceeds. In order of their decreasing effect on the reaction rate, this sequence is as follows (references 15 and 143):

$$H_2SO_4 > HNO_3 >> CH_3NO_2 > CH_3CO_2H >> H_2O$$

The effect of constitution of the aromatic compounds on the reaction order and mechanism may also be graded according to the relative rates at which variously substituted aromatic compounds would be attacked under comparable conditions. The order of the substituent effect is approximately the same as that to be expected from considerations of the activation or deactivation of the benzene ring by these groups. From competition experiments, the following sequence has been set up (references 15 and 143):

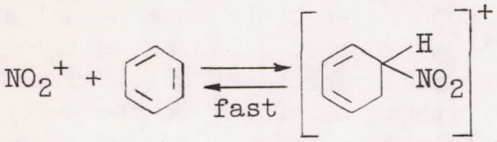
$$CH_3-,\ C_2H_5- > H- > F-,\ I- > Cl-,\ Br- > -CO_2Et > -SO_3H > -NO_2$$

The highly activating substituent groups such as the hydroxyl or the amino group cannot be included in this series since nitrations of these compounds seem to proceed by more complex mechanisms (references 144 to 147). Reactions involving these groups are discussed in the latter part of this section.

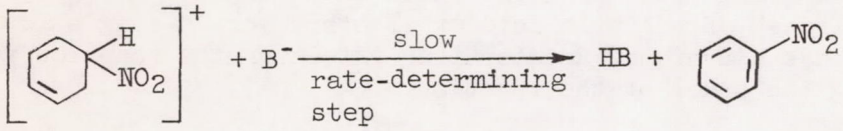
In an anhydrous or nearly anhydrous medium, nitration of aromatic compounds by nitric acid proceeds through the formation of the nitronium ion, $NO_2^+$. The presence of this ion in concentrated nitric acid is discussed in the preceding section (reference 15).

In general, the nitration of aromatic hydrocarbons is a bimolecular reaction. The order of reaction, however, is a function of the solvent medium as well as of concentration of the reactants. Thus, in an excess of sulfuric acid, the reaction is second order; in nitric acid, it is first order; and in organic solvents, with an excess of nitric acid, it varies between zero and one, depending on the reactivity of the hydrocarbon being nitrated (reference 15).

In the recent literature, two over-all mechanisms for aromatic nitrations are advanced. The first of these (references 148 to 151) visualizes the following processes, benzene being used here as a simple example of an aromatic hydrocarbon undergoing nitration. The nitronium ion attacks the benzene molecule by a rapid reversible reaction to form a transition complex. In the presence of a base in the medium, this complex extracts a proton and forms nitrobenzene. Schematically, this reaction may be represented as follows:




(45)

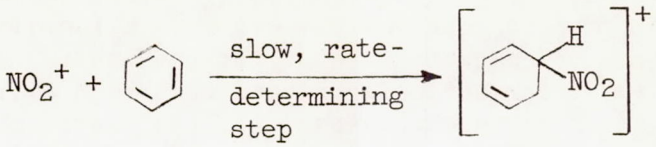



(46)

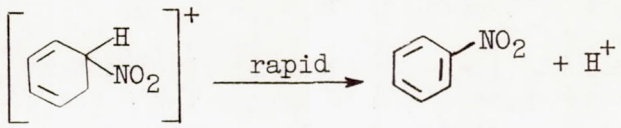
where $B^-$ represents a base.

This mechanism has been termed "termolecular" (reference 15) since it involves three original species undergoing covalency changes. The necessary base may be furnished by the bisulfate or the nitrate ions in the solution.

The alternative mechanism (reference 15) proposes that the attack of the nitronium ion on benzene or on other aromatic compounds is the slow, rate-determining step. The loss of the proton from the activated complex formed in this manner is considered a fast reaction. This mechanism is termed "bimolecular". It accounts readily for the various observations made of the effects of solvents and small amounts of additives to the reaction mixture. Furthermore, recent work on the nitration of aromatic compounds containing tritium has indicated that the proton loss is indeed a reaction which does not contribute to the over-all kinetics of the reaction (references 152 and 153). Such bimolecular mechanisms may be represented by the equations:




(47)




(48)

In this case, the ejection of a proton from the transition complex is rapid and kinetically insignificant.

Aromatic nitrations are profoundly influenced by the presence of small concentrations of other constituents in the reaction mixture. In the case of aromatic substances other than phenol and aniline derivatives, the presence of nitrous acid has an inhibiting effect on the reaction rate even in small concentrations. Although it affects the rate of the reaction, it has no effect on the order of the reaction. In nitration media which are devoid of sulfuric acid such as those using pure nitric acid or nitric acid in an organic solvent, the addition of traces of sulfuric acid or of other very strong acids as a catalyst has a profound accelerating effect on the reaction rate without affecting the order of the reaction.

Additions of small amounts of alkali metal salts such as potassium chloride or potassium bisulphate have only a slightly inhibiting influence on the reaction rates of the nitration. In contrast, additions of nitrates, particularly alkali metal nitrates or ammonium nitrate, to the reaction mixture have a very decided negative catalytic effect on the reaction rates. These observations are discussed in detail in reference 15.

The nitration of highly reactive aromatic compounds such as phenols, aniline, or their derivatives proceeds by a special mechanism (references 145 and 146). Although the reaction follows essentially zero order kinetics in a medium containing an excess of nitric acid, the effect of nitrous acid is one of accelerating this reaction whereas, as pointed out previously, this acid ordinarily inhibits nitration.

In the case of zero order nitration of aromatic hydrocarbons such as toluene in an excess of nitric acid, the effect of nitrous acid on the rate constant is given by:

$$\text{rate} = \frac{[\text{ArH}]^0}{a + b\,[\text{HNO}_2]^{1/2}} \tag{49}$$

where the constants a and b represent complex functions of the nitric acid concentration and of the temperature (reference 143).

The nitration of phenols and aromatic amines in an excess of nitric acid seems to require the presence of nitrous acid. The effect of nitrous acid concentration on the rate constant is given in the limiting cases by:

$$\text{rate} = K\,[\text{ArH}]\,[\text{HNO}_2] \tag{50}$$

The complexity of the kinetics of these nitrations arises from a superimposition of these two expressions. The mechanisms of these reactions are discussed in references 144 and 147.

In a rocket engine, it is unlikely that aromatic nitrations are significant in the relatively low-temperature preignition reactions unless the time of contact prior to ignition (ignition delay) is quite long. In the latter case, it is possible that some nitro compounds are formed which may subsequently detonate.

In the combustion process, it is also unlikely that aromatic nitration is significant compared with oxidation since it is difficult to prevent oxidation of phenols and aromatic amines by concentrated nitric acid even at temperatures much lower than the combustion temperatures.

## Oxidation Reactions

In the case of nitric acid oxidation, the nature of the material oxidized and the exact conditions of the reaction have a profound influence on the composition of the products derived from the acid. In order of decreasing degree of oxidation, the following substances may be among the products:

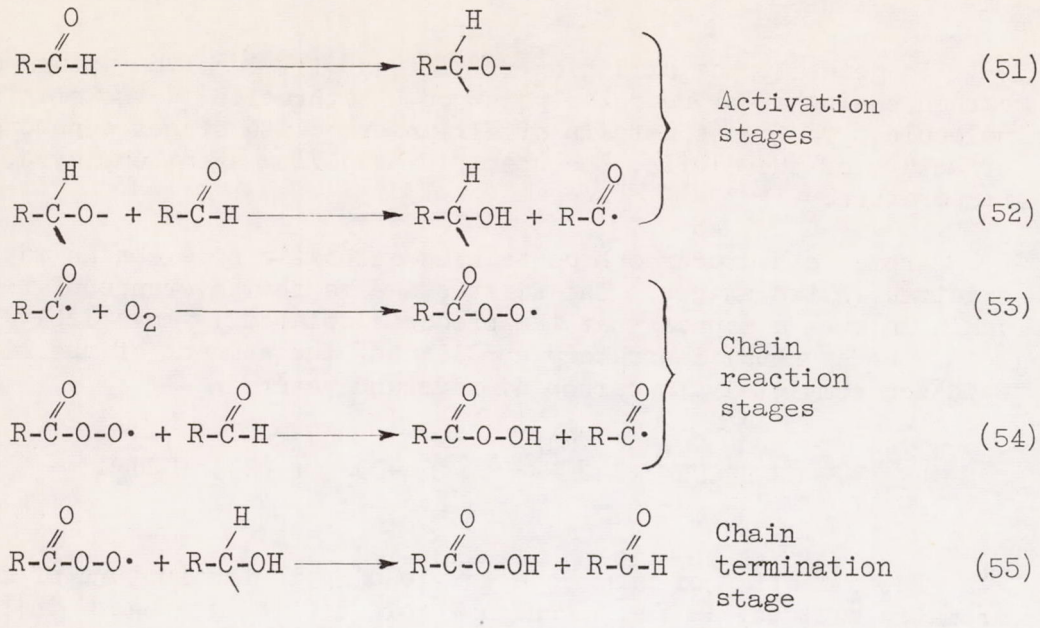
$$NO_2,\ NO,\ N_2O,\ N_2,\ N_2H_4,\ \text{and}\ NH_3$$

A generalized discussion of the subject is difficult because the oxidation of each compound differs in many significant respects even among members of the same general class. For example, problems arise as to the order in which various atoms in the molecule may be attacked by the oxidizing agent. Even in a homologous series of compounds, questions arise such as: (1) at which carbon atom does the attack

begin, (2) at what stage of the oxidation does attack of various functional groups occur, (3) at what time does the carbon skeleton break down, (4) into what units does this skeleton break down, (5) how reactive are these smaller units, and (6) how rapidly do they react further with the oxidizing agent to afford the ultimate oxidation products of pure organic compounds.

The complexity of the problem of evaluating the factors that concern the determination of the reaction rates in oxidation-reduction reactions has been indicated in reference 154. According to this reference, the rate of oxidation is dependent not only on the nature and constitutions of the oxidizing agent and reducing agent, but also on (1) the solvent; (2) the pH of the solution, which may be interpreted in a nonaqueous system as the Hammett acidity function ($H_0$) of the solution (reference 137); (3) the temperature; (4) the effects of concentrations of the various reagents; (5) the difference in the oxidation-reduction potential of the reagents; (6) the influence of certain added ions that may bring about catalytic effects; and (7) the influence of the dissociation of various reactants. In an aqueous system, oxidation-reduction potentials usually permit prediction as to the possibility of a reaction; however, they do not predict the rate at which the reaction will proceed, if at all. The term oxidation-reduction potential refers usually to reversible chemical reactions. In many cases in a rocket engine, the molecules are completely destroyed to form smaller units. The final oxidation steps are therefore of an irreversible nature; consequently, ordinary oxidation-reduction potentials for rocket processes may be of questionable value. The processes which form the ultimate oxidation products of organic compounds, that is, carbon dioxide, water, nitrogen and its oxides, are sufficiently subject to debate in the literature that no positive evaluation can be made at this time.

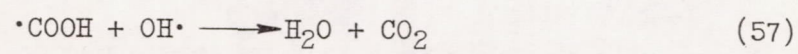
In recent years, a large amount of evidence has been accumulated to show that several oxidation reactions have the removal of atomic hydrogen or the addition of neutral hydroxyl radicals as initial stages; that is, they are of a nonionic or free radical character (reference 155). Such free radical reactions may become chain reactions. A simple example is the autoxidation of benzaldehyde in the presence of oxygen. In this process, a benzaldehyde molecule loses one hydrogen atom. The resultant radical reacts in such a manner as to regenerate the reactive radical along with other products. The process thus becomes a chain reaction (reference 156).




Analogous oxidation reactions may be written for liquid hydrocarbons as well as for aldehydes. This type of mechanism seems to be particularly suitable to explain the action of oxidizing agents such as lead tetra-acetate, chromic oxide, potassium permanganate, and periodic acid. Whether it is applicable to oxidizing agents such as nitric acid cannot be ascertained positively from the literature. Oxides may act as abstractors of hydrogen in oxidation reactions only if they contain double covalent bonds and no coordinate links (reference 155). Since nitric acid is usually considered to contain a coordinate link, it is possible that this acid would behave differently in oxidations.

In free radical oxidations, the formation of carbon dioxide and water may be assumed to proceed by such steps as these: At some stage of the oxidation, a carboxylic acid, which is the highest oxidation stage of a carbon atom in a molecule prior to rupture of the carbon linkage, is formed. The interaction of a carboxylic acid with a hydroxyl radical will form carbon dioxide and water (reference 157).

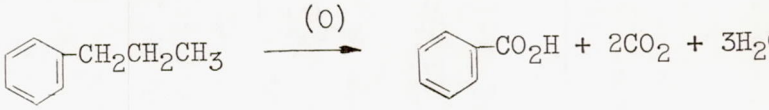



Alcohols, ethers, and ketones also may be oxidized by reagents like chromic oxide. The primary attack on the organic molecule is probably on the functional groups in the cases of alcohols and ethers. The oxidative cleavage of ketones probably takes place at the activated methylene groups adjacent to the carbonyl group. The mechanism of these reactions may involve the intermediate formation of free radicals (reference 158).

In general, the oxidation of olefins will involve rupture of the carbon chains at or near the point of unsaturation in the original molecule. The exact details of all intermediate stages depend on the structure of the olefin, the specific oxidizing agent employed, and the temperature.

Aromatic hydrocarbons containing aliphatic side chains may be oxidized in two stages. The first stage is the severance of the side chain in such a manner that the product isolated is invariably benzoic acid. Under usual laboratory conditions, the remnant of the side chain oxidizes completely to carbon dioxide and water.




(58)

The oxidation of benzoic acid, leading to the rupture of the aromatic nucleus, is the second and more difficult stage. Only the most vigorous conditions will suffice. If other reactive substituents are present in the aromatic ring system, oxidation of the ring may be facilitated considerably.

Aromatic amines are oxidized quite readily. The process, however, is of a highly complex nature. The oxidation of aniline, for example, has been studied in great detail (references 159 and 160). These studies have shown that the nature of the oxidizing agent is of particular importance. For example, oxidizing agents like hydrogen peroxide and permonosulfuric acid, $H_2SO_5$, donate oxygen to the aniline molecule, while a second class of oxidizing agents, which contains the majority of the oxidizing agents used in technical procedures for the oxidation of aniline, act by the extraction of hydrogen from the amino group to form free radicals. Typical examples of reagents of this second class are: chromic oxide, perdisulfuric acid, and lead peroxide.

By boiling with concentrated nitric acid, mercaptans are oxidized to the corresponding sulfonic acids:

$$R\text{-}SH \xrightarrow{[O]} R\text{-}SO_3H \qquad (59)$$

It is quite probable that this process proceeds step-wise with the addition of one oxygen atom at a time. If reaction conditions become even more vigorous, the sulfur atom may split away in the form of sulfur dioxide or sulfur trioxide. The organic remnant will probably undergo oxidation similar to analogous fragments obtained in the oxidation of alcohols.

The oxidation of mercaptans can be promoted effectively by the presence of catalytic amounts of copper- or iron-containing compounds (reference 161). The oxidation of aniline derivatives is also promoted by compounds of copper and of mercury (reference 162). Either copper sulfate or mercuric sulfate may be used, each having a definite catalytic effect on the oxidation of aniline. In the presence of a mixture of cupric and mercuric sulfates, the catalytic effect is considerably enhanced. This catalytic effect is not merely the sum of the effects expected from the quantities of the individual catalysts added but is definitely synergistic.

Although the oxidation of many of the substances used in a rocket engine has been studied, the information available on the use of nitric acid as the oxidizing agent is limited. Further research is needed to establish the rates of oxidation of concentrated nitric acid with various classes of fuels. Determination of the effects of reaction chamber volume, surface condition, catalysts, and turbulence on the rate of reaction should be made. Study is also needed on means for preventing detonations in the reaction mixtures, possibly through identification of intermediate products.

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TABLE I - CORROSION RATES OF TYPES 347 AND 347 EXTRA-LOW-CARBON STAINLESS STEELS IN BOILING 65-PERCENT NITRIC ACID (REFERENCE 47)

Averages of five 48-hr tests

| History of material | | Corrosion rate (mils/yr) | |
|---|---|---|---|
| Heat treatment | Atmosphere during heating | 347 | 347 Extra-low carbon |
| 2400° F 1/2 hr; water quench | Air | 10 | 6 |
| 2400° F 1/2 hr; water quench | Argon | 9 | 5 |
| 1950° F 1/2 hr; water quench | Air | 19 | 5 |
| 1750° F 1/2 hr; water quench | Air | 13 | 5 |
| 2400° F 1/2 hr; water quench; 1200° F 2 hr; air cooled | Air | 330 | 14 |
| 2400° F 1/2 hr; water quench; 1200° F 2 hr; air cooled | Argon | 94 | 9 |
| 1950° F 1/2 hr; water quench; 1200° F 2 hr; air cooled | Air | 34 | 24 |
| 1750° F 1/2 hr; water quench; 1200° F 2 hr; air cooled | Air | 23 | 9 |

TABLE II - EFFECT OF HYDRATED ALUMINUM NITRATE ADDITION ON CORROSION RATE OF TYPE 347 STAINLESS STEEL IN RED FUMING NITRIC ACID AT 160° F (REFERENCE 45)

| Sample condition | Additive (percent by wt) | | | |
|---|---|---|---|---|
| | 0.0 | 0.0001 | 0.01 | 1.0 |
| | Corrosion rate (mils/yr) | | | |
| [a]As welded | 160 | 205 | 162 | 11 |
| [b]Welded + 2 hr at 1200° F | 734 | 860 | 835 | 28 |
| [a]Welded + 1/2 hr at 1650° F | 165 | 206 | 178 | 13 |

[a]Exhibited general corrosion
[b]Exhibited severe intergranular attack except in the case of 1.0 percent additive

TABLE III - EFFECT OF ADDITION OF HYDRATED ALUMINUM NITRATE OR WATER EQUIVALENT TO THAT CONTAINED IN HYDRATED ALUMINUM NITRATE ON CORROSION RATE OF TYPE 347 STAINLESS STEEL AT 160° F (REFERENCE 47)

[Averages of five 48-hour tests]

| Test solution | Corrosion rate (mils/yr) |
|---|---|
| 1. WFNA + 1 percent hydrated aluminum nitrate | 47 |
| 2. WFNA + water equivalent in solution 1 | 40 |
| 3. RFNA + 1 percent hydrated aluminum nitrate | 53 |
| 4. RFNA + water equivalent in solution 3 | 20 |
| 5. WFNA (no additive) | 130 |

TABLE IV - ACID PRESSURES IN GLASS APPARATUS AT 122° F

(REFERENCE 80)

| Initial acid composition (percent) | | | Ullage (percent) | Initial rate of pressure rise (lb/sq in./hr) | Time (hr) | Pressure at end of time (lb/sq in. gage) |
|---|---|---|---|---|---|---|
| $HNO_3$ | $H_2O$ | $NO_2$ | | | | |
| 100 | 0 | 0 | 6.3 | 10.9 | 320 | 1230 |
| 100 | 0 | 0 | 12.5 | 8.2 | 400 | 900 |
| 99.2 | 0.8 | 0 | 7.8 | 2.1 | 950 | 893 |
| 98.6 | 1.4 | 0 | 10.5 | 1.6 | 300 | 514 |
| 82.4 | 0 | 17.6 | 3.8 | 6.5 | 450 | 473 |

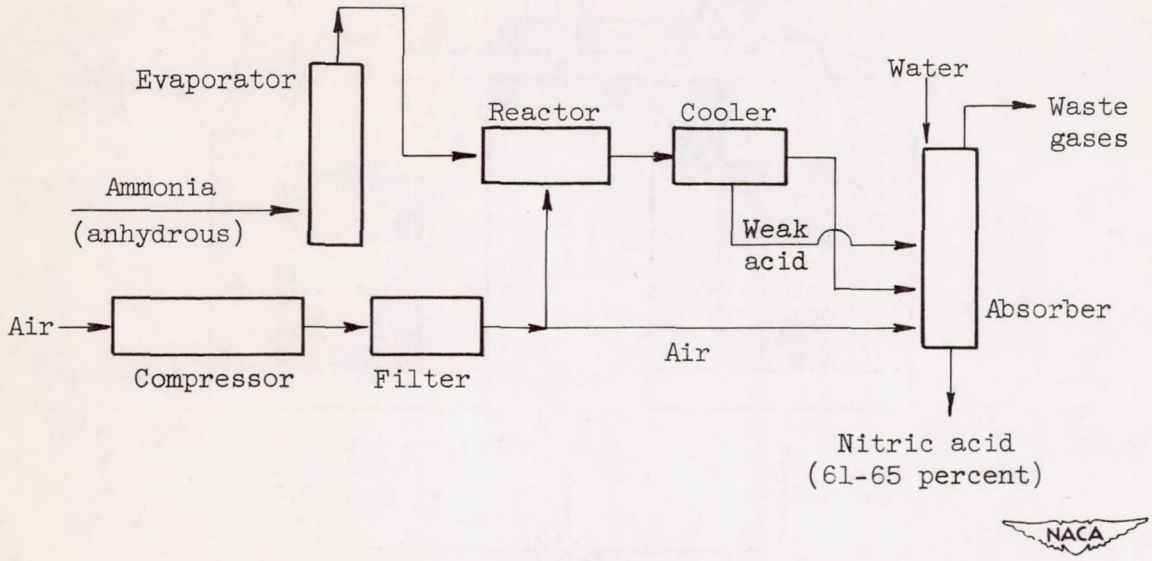



Figure 1. - Ammonia oxidation process (reference 4).

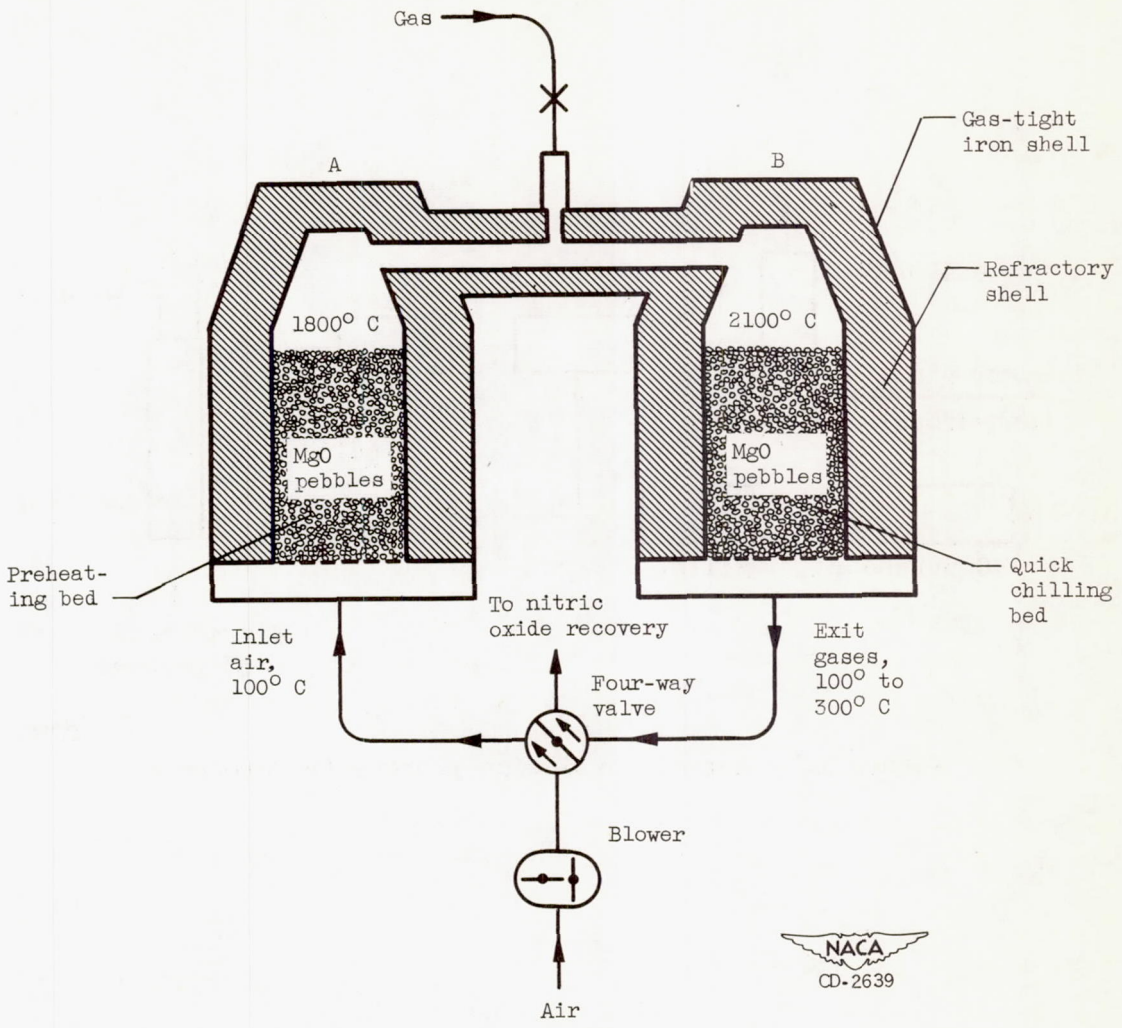



Figure 2. - Apparatus for direct fixation of nitrogen as nitric oxide (reference 8).

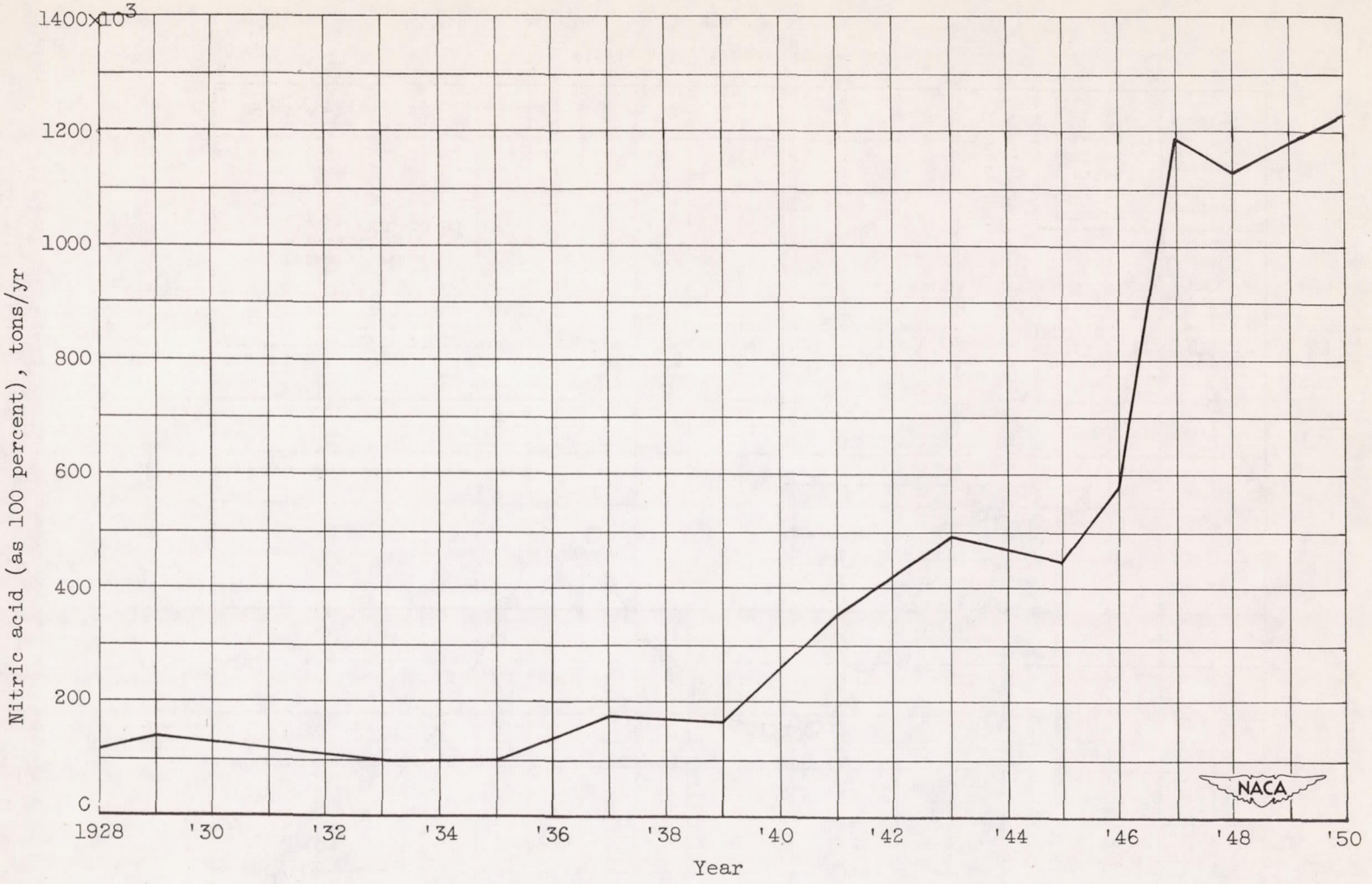
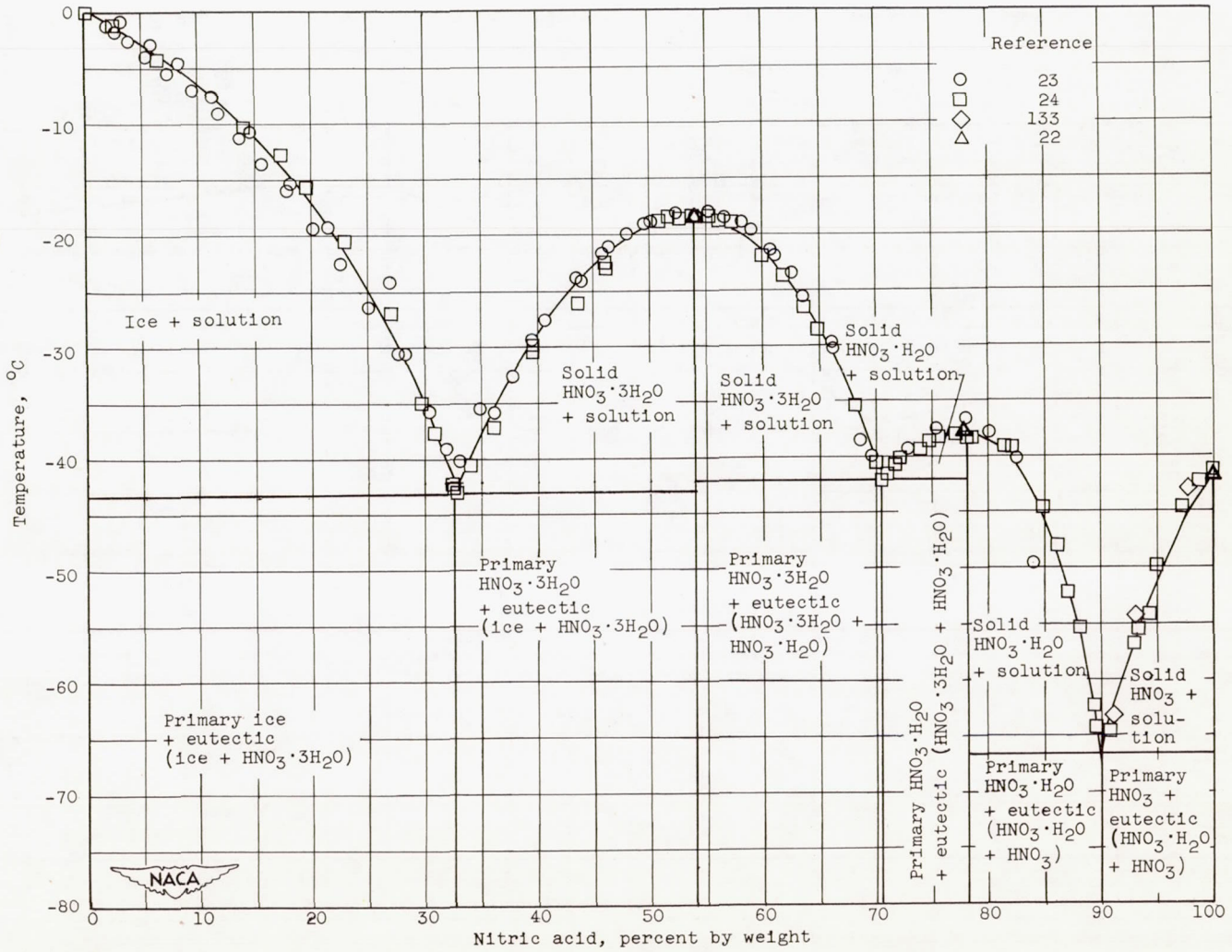
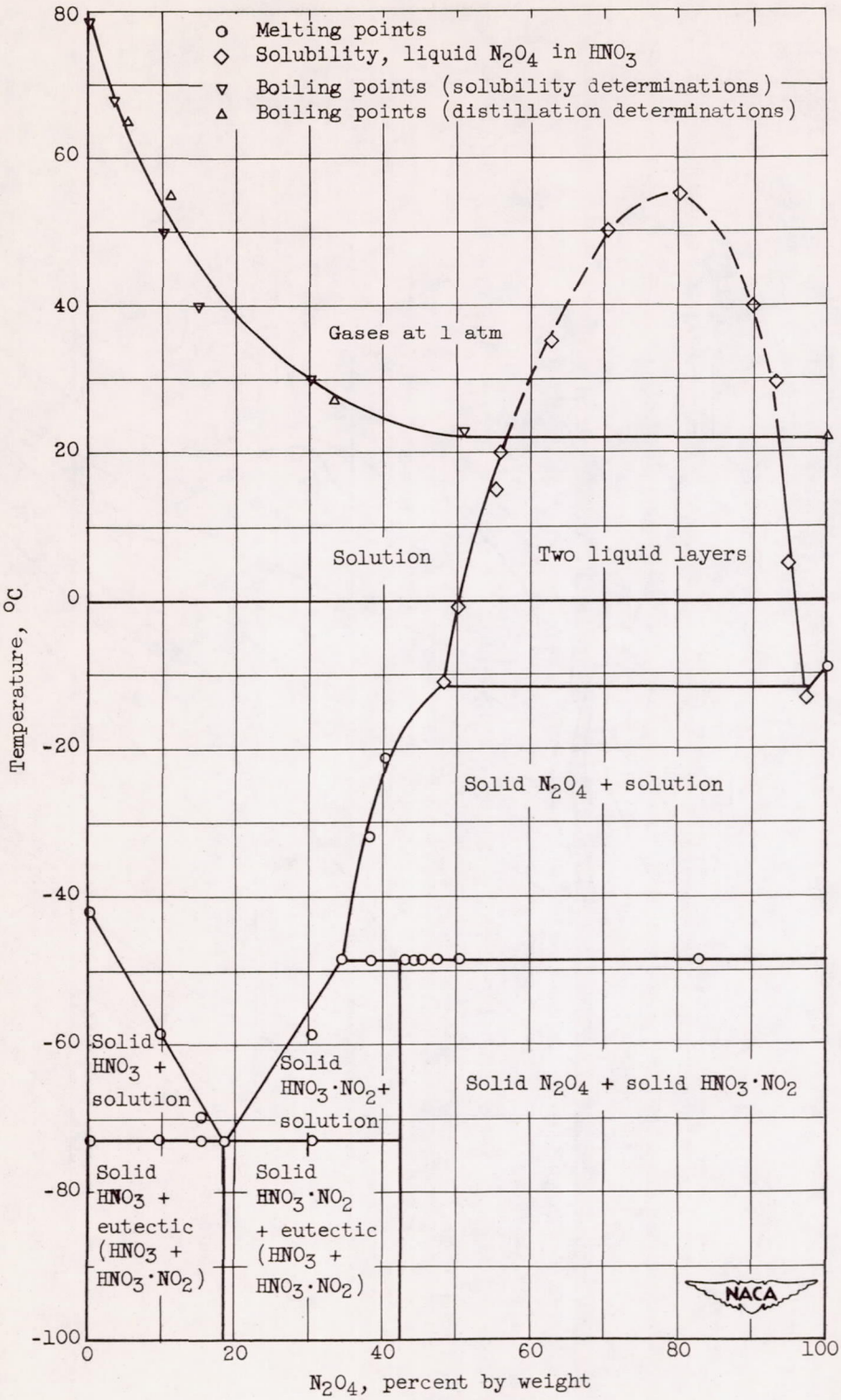



Figure 3. - Commercial production of nitric acid (references 4 and 10).




(a) $HNO_3$, $H_2O$.

Figure 4. - Phase diagrams.




(b) $HNO_3$, $N_2O_4$ (reference 25).

Figure 4. - Concluded. Phase diagrams.

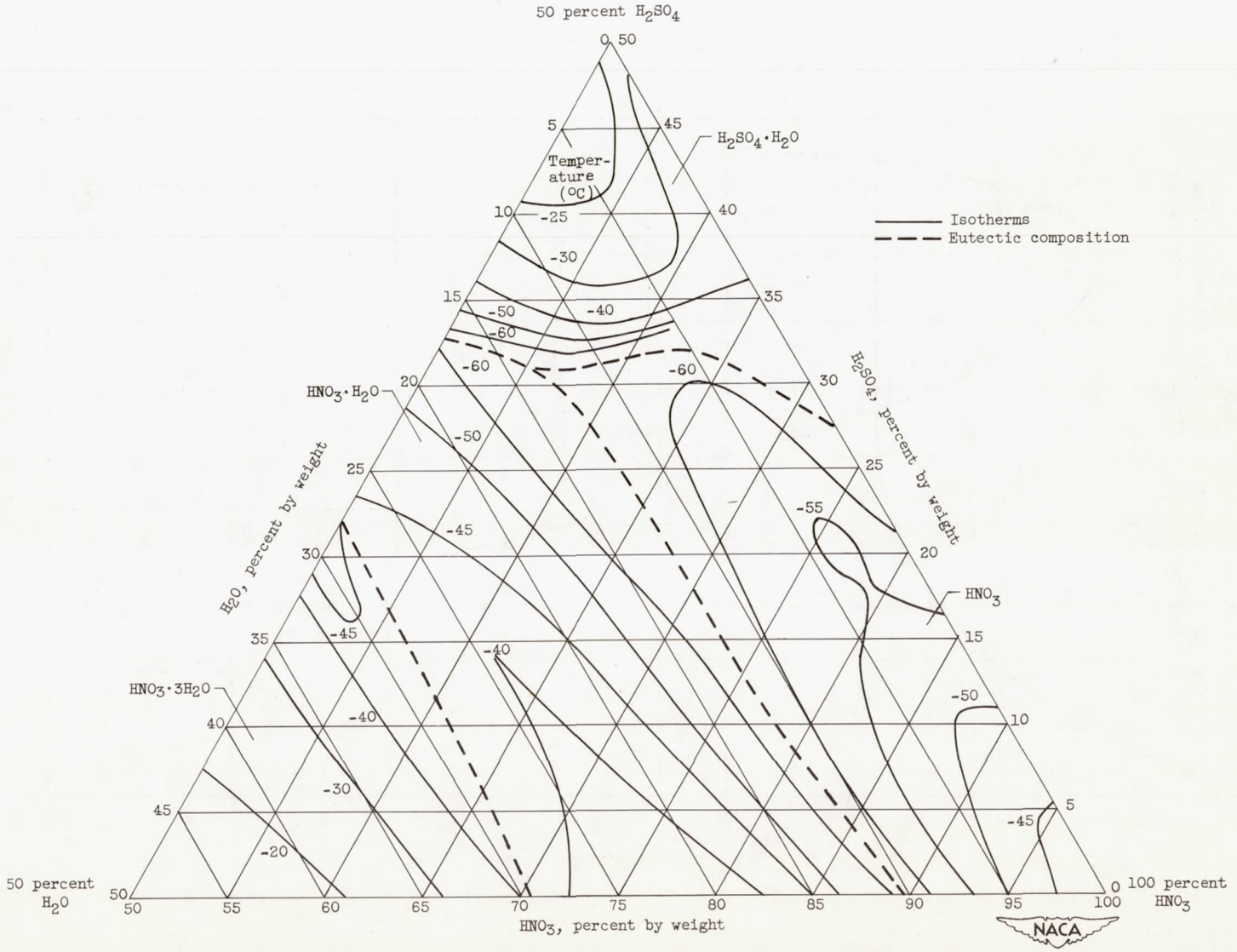



Figure 5. - Melting points for $HNO_3$, $H_2SO_4$, $H_2O$ system. (Plot constructed from data of reference 26.)

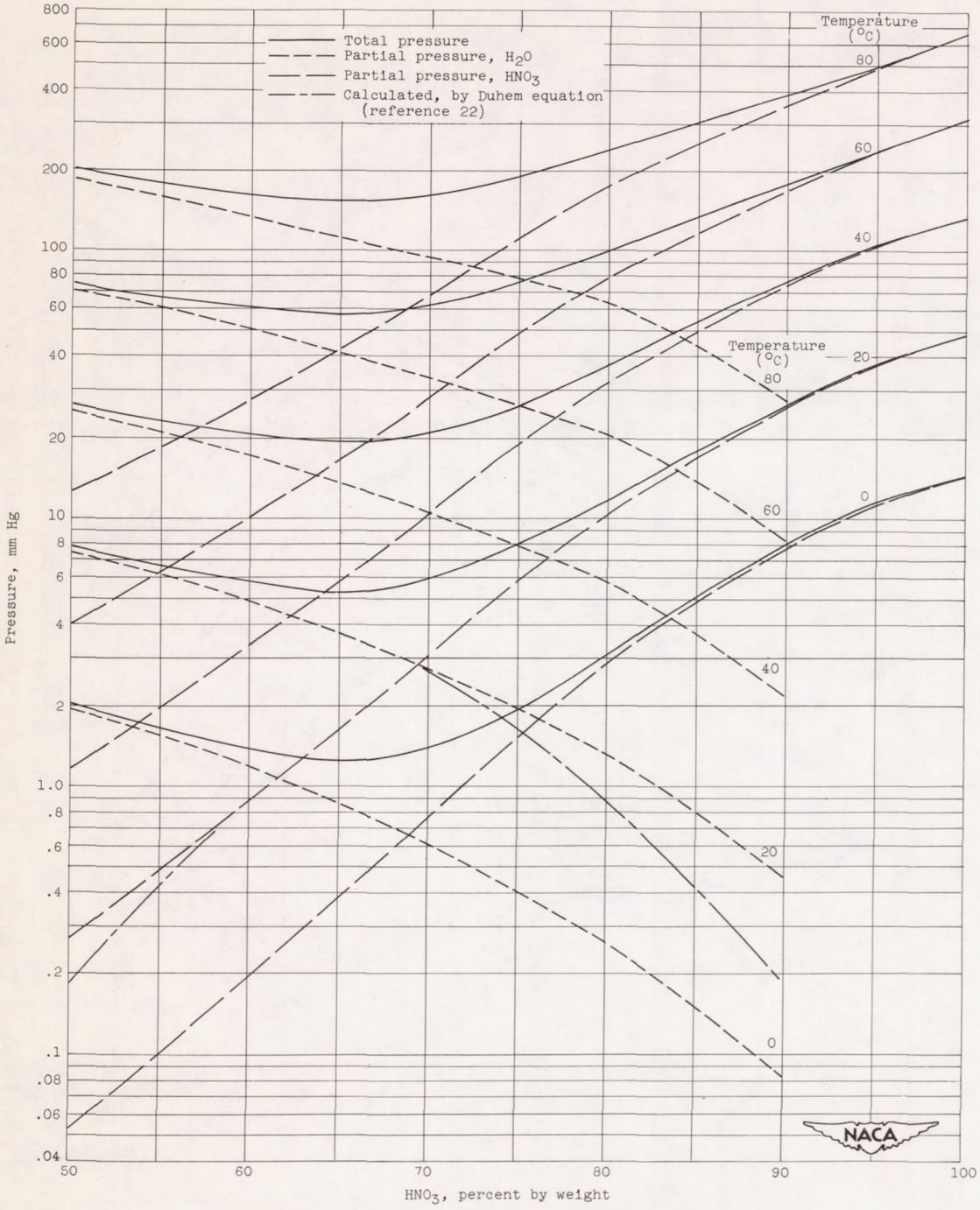
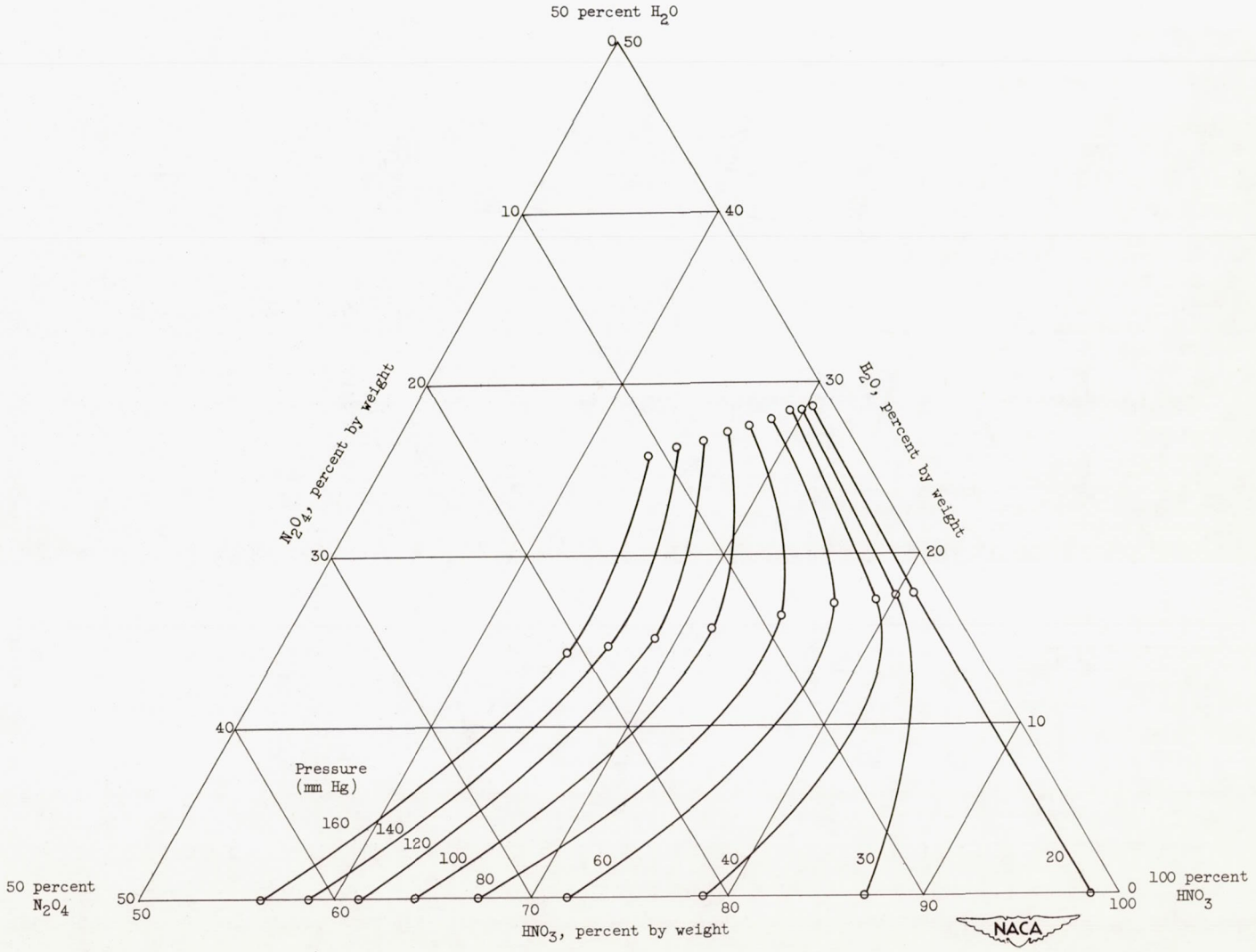
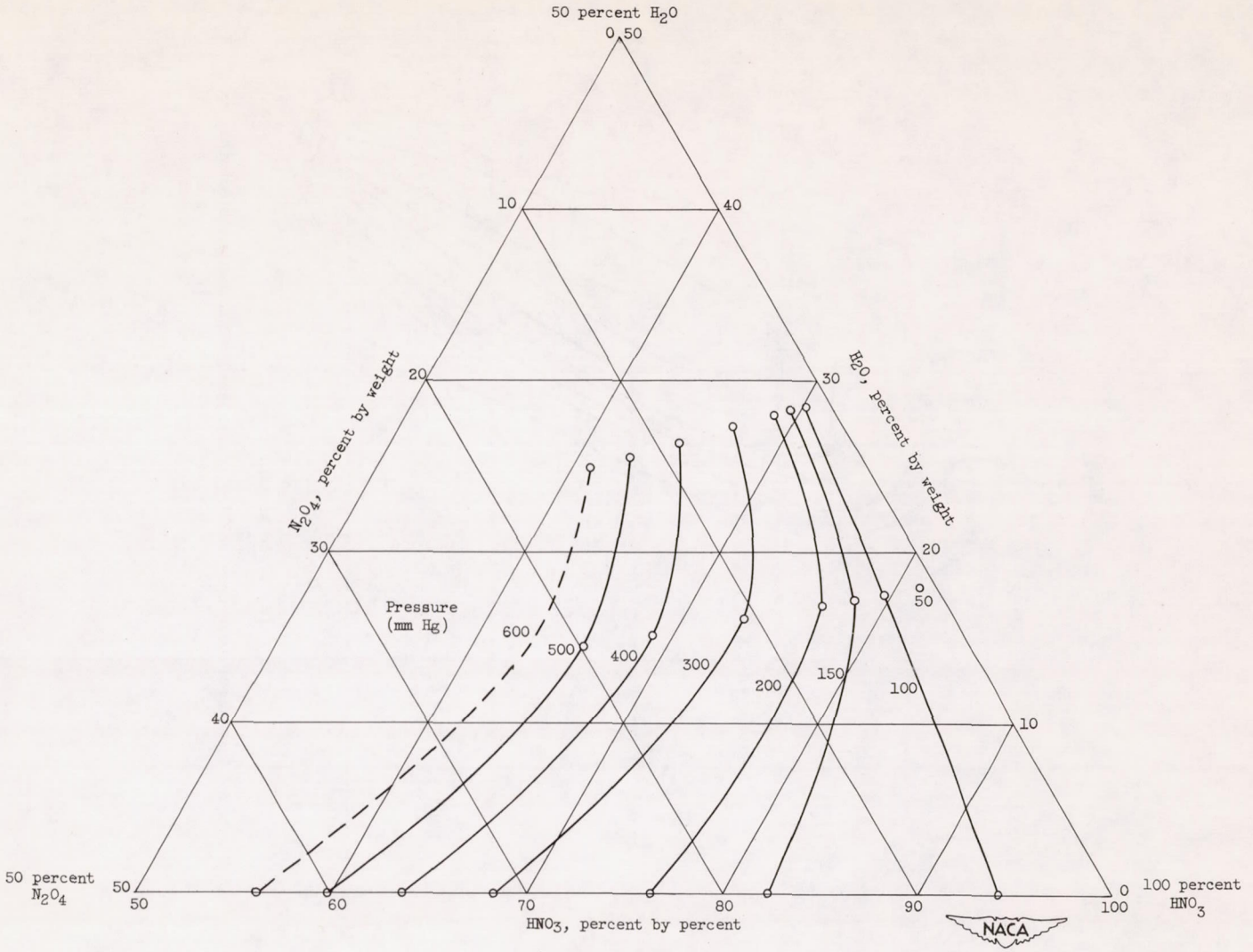



Figure 6. - Total and partial vapor pressures for $HNO_3$, $H_2O$ system.



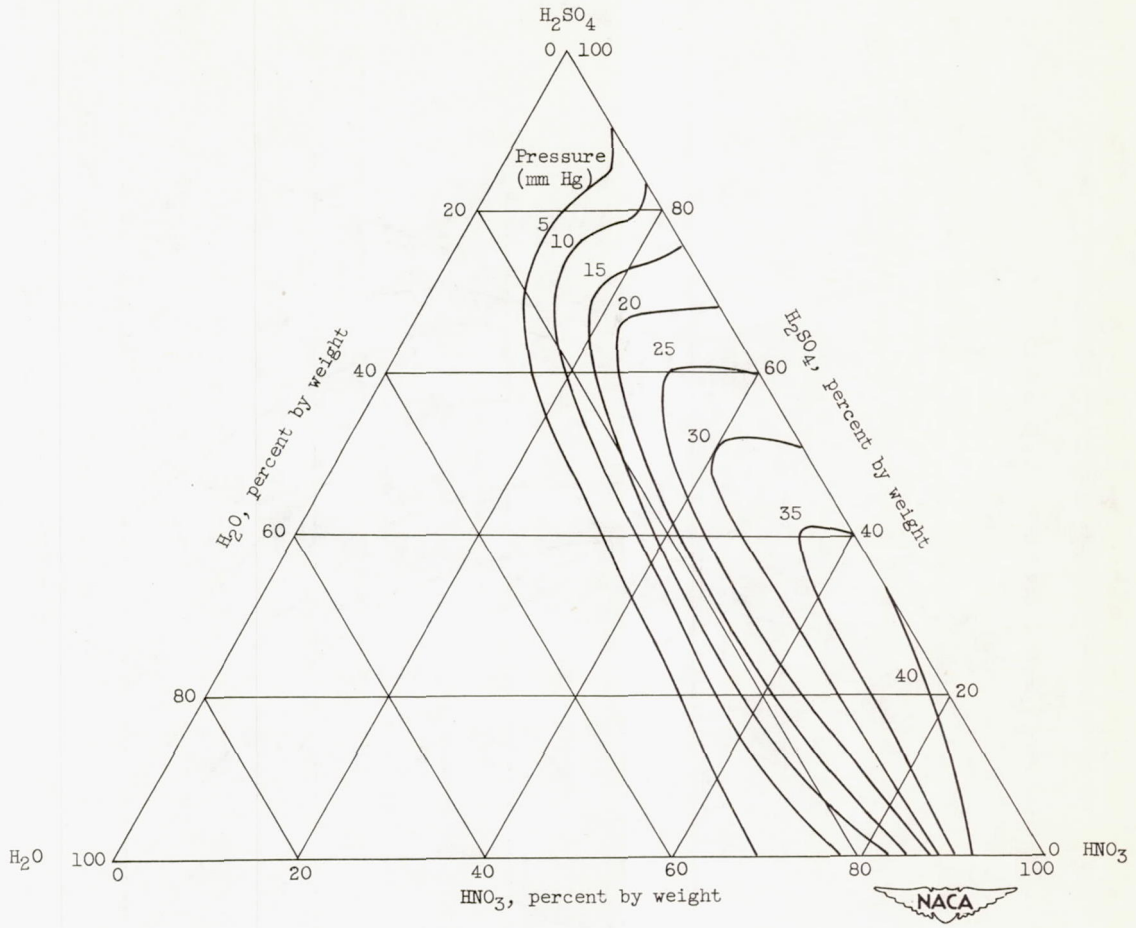

(a) Temperature, 0° C.

Figure 7. - Vapor pressures of $HNO_3$, $N_2O_4$, $H_2O$ system. (Plots constructed from data of reference 28.)



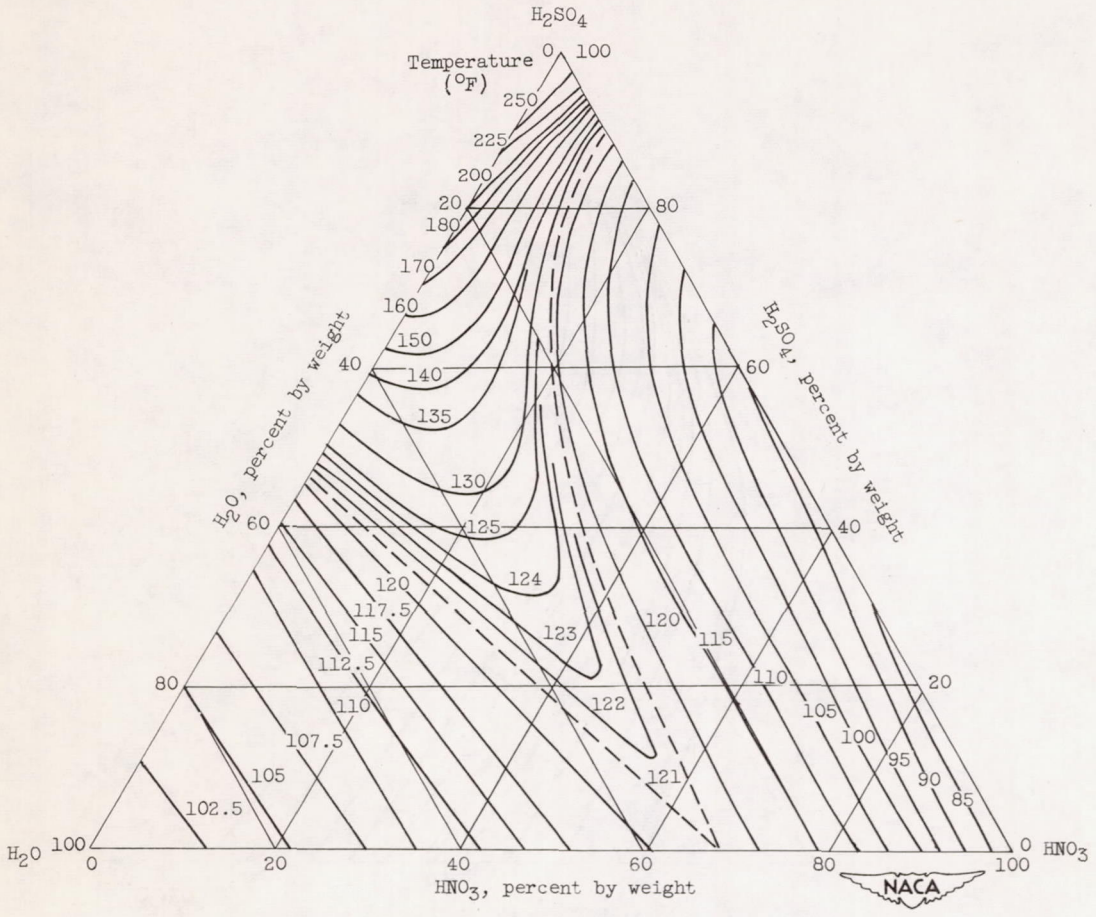

(b) Temperature, 25° C.

Figure 7. - Concluded. Vapor pressures of $HNO_3$, $N_2O_4$, $H_2O$ system. (Plots constructed from data of reference 28.)



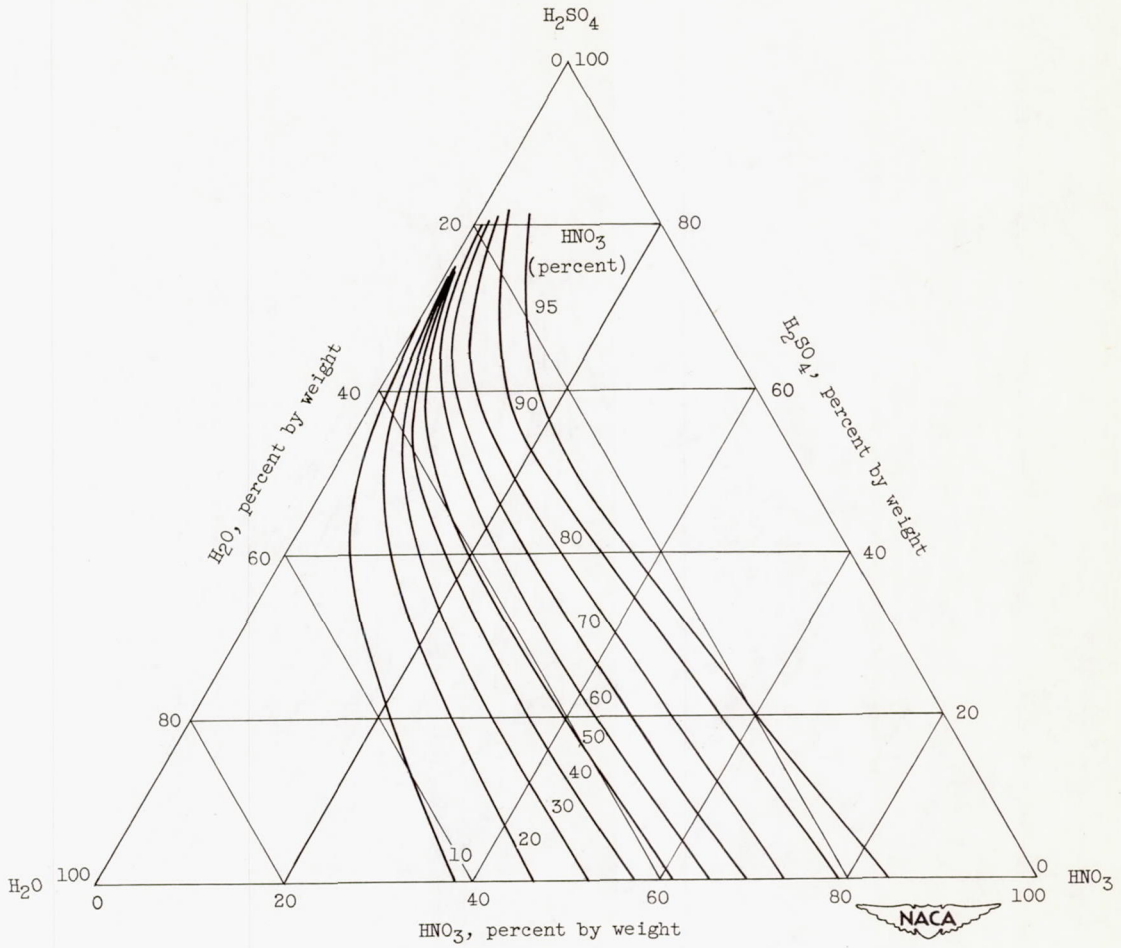

(a) Vapor pressures at 25° C.

Figure 8. - Vapor pressure, boiling points, and vapor compositions for $HNO_3$, $H_2SO_4$, $H_2O$ system (reference 19).



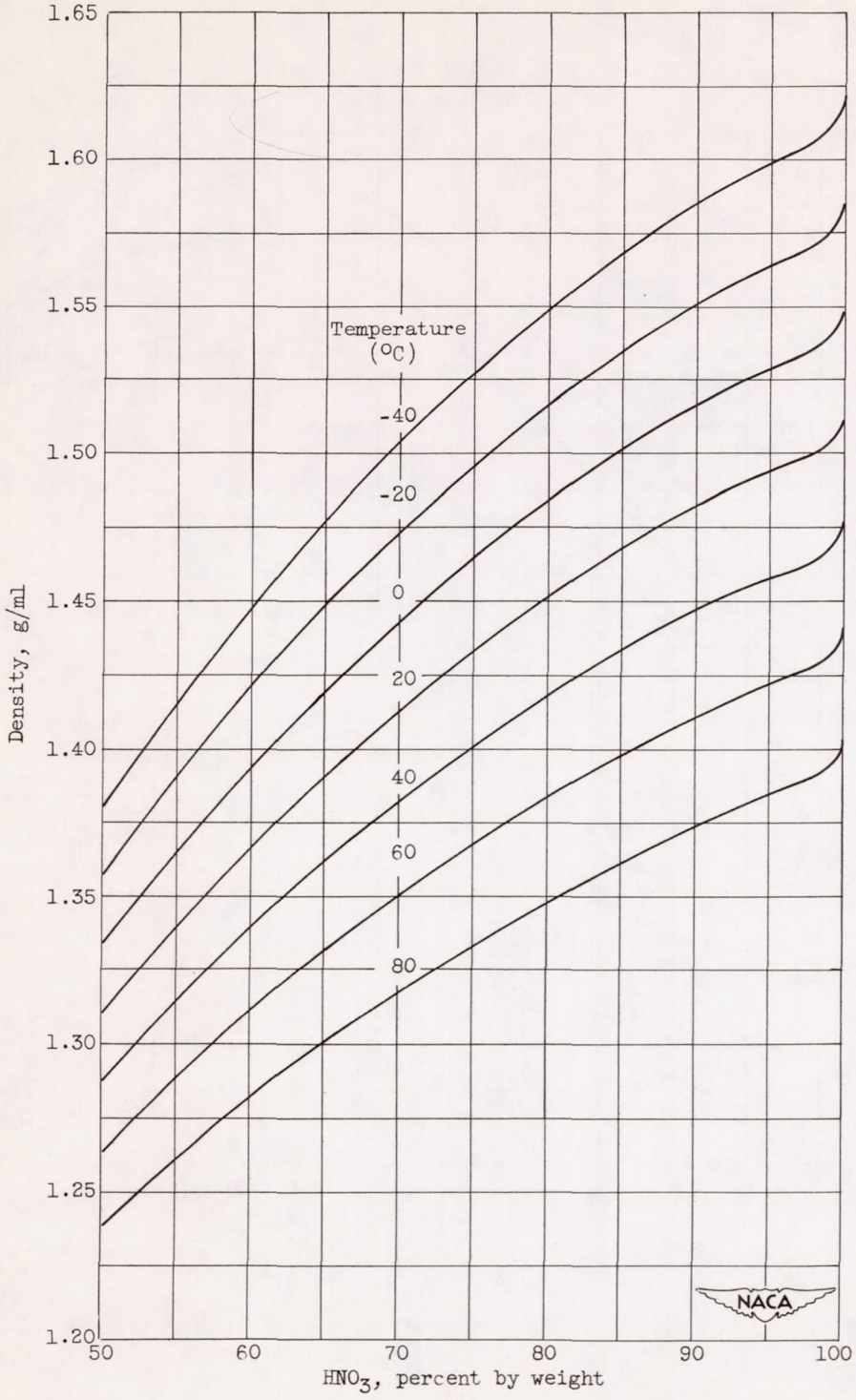

(b) Boiling points at 760 millimeters of mercury pressure.

Figure 8. - Continued. Vapor pressure, boiling points, and vapor compositions for $HNO_3$, $H_2SO_4$, $H_2O$ system (reference 19).



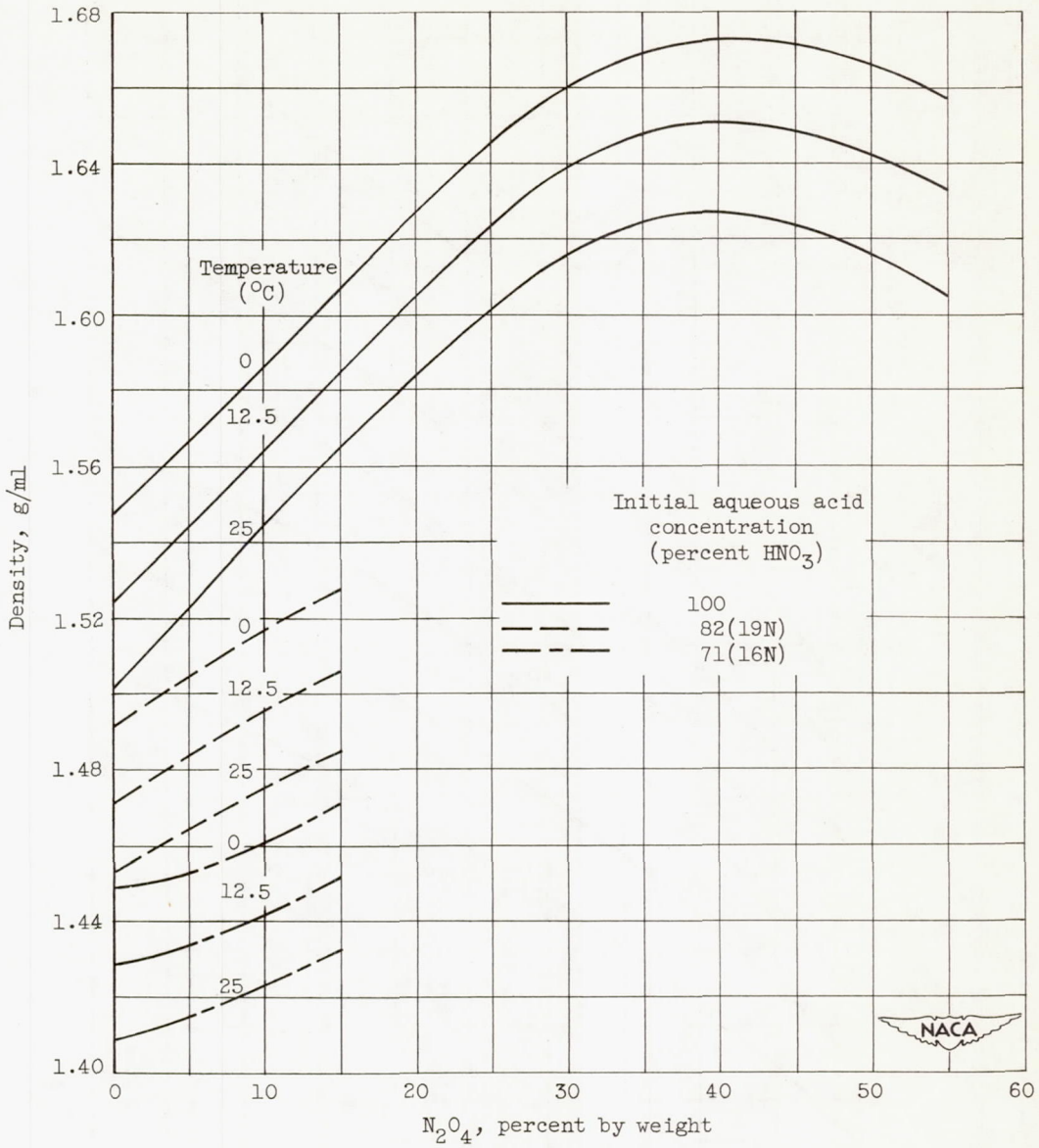

(c) Vapor compositions at 760 millimeters of mercury pressure.

Figure 8. - Concluded. Vapor pressure, boiling points, and vapor compositions for $HNO_3$, $H_2SO_4$, $H_2O$ system (reference 19).



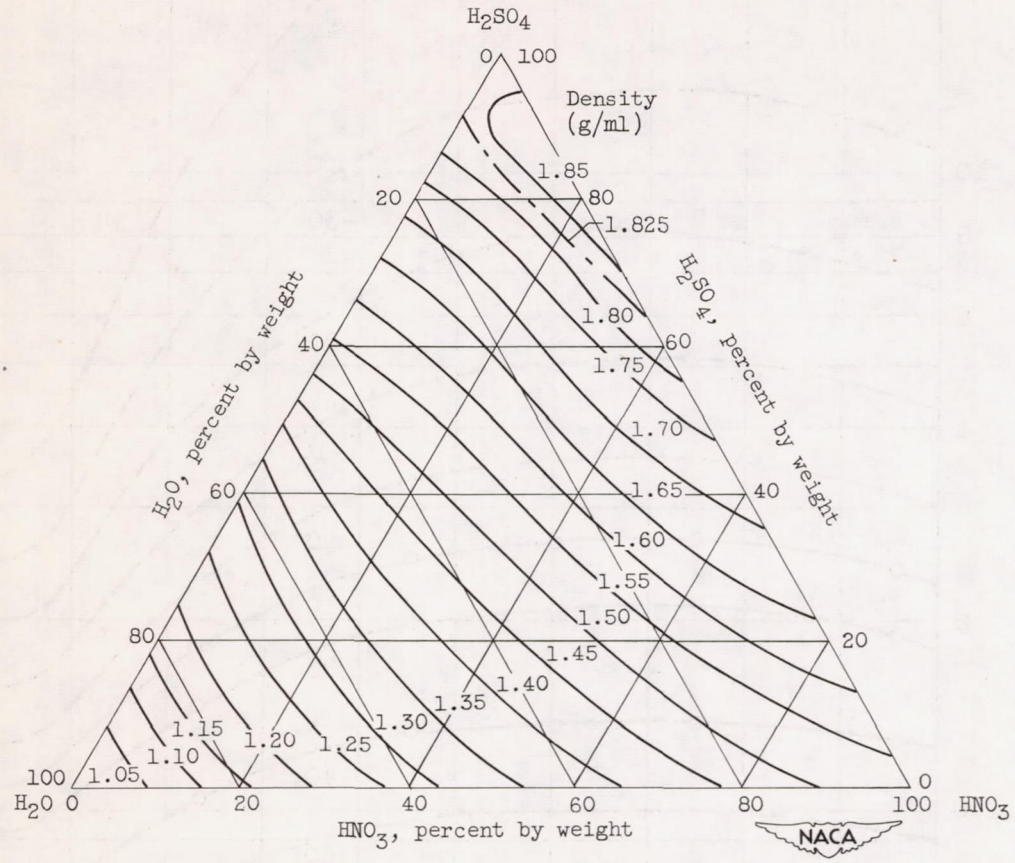

(a) $HNO_3$, $H_2O$.

Figure 9. - Densities for various systems.




(b) $HNO_3$, $N_2O_4$, $H_2O$ (reference 28).

Figure 9. - Continued. Densities for various systems.




(c) $HNO_3$, $H_2SO_4$, $H_2O$ (reference 33). Temperature, 15° C.

Figure 9. - Concluded. Densities for various systems.

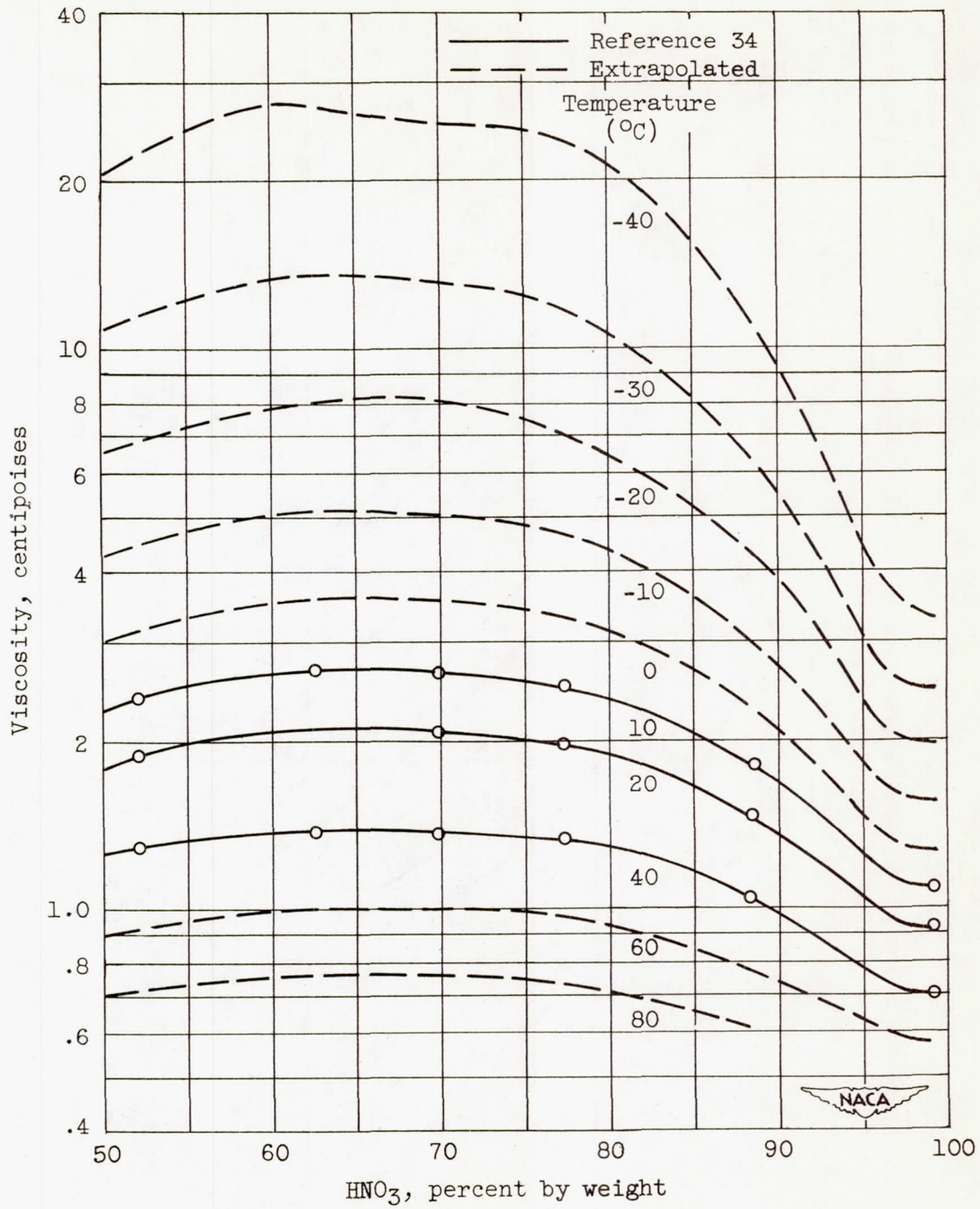
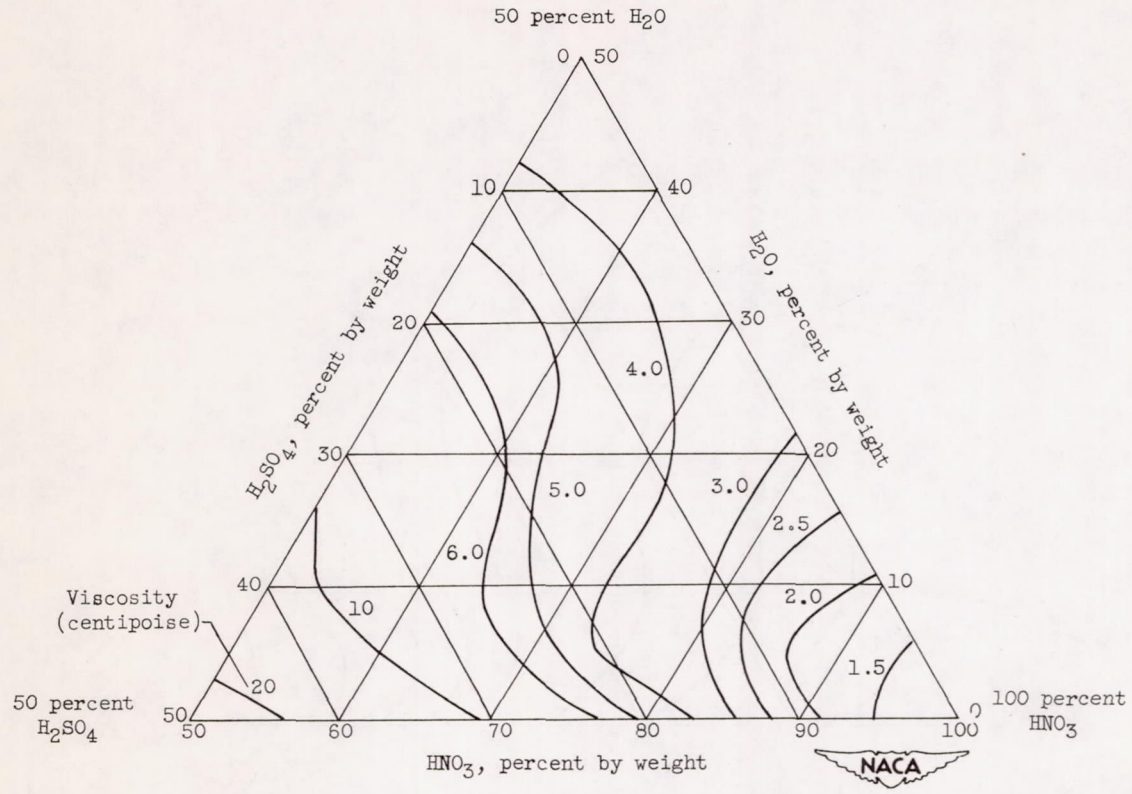
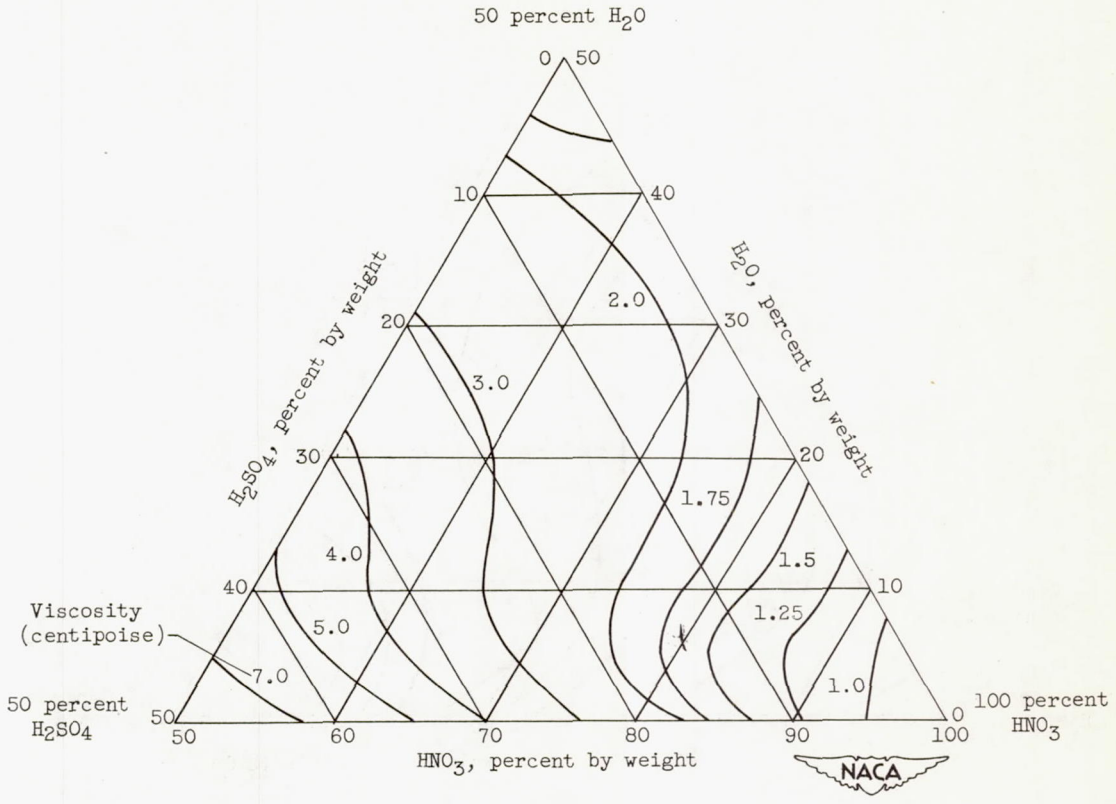



Figure 10. - Viscosities for $HNO_3$, $H_2O$ system.



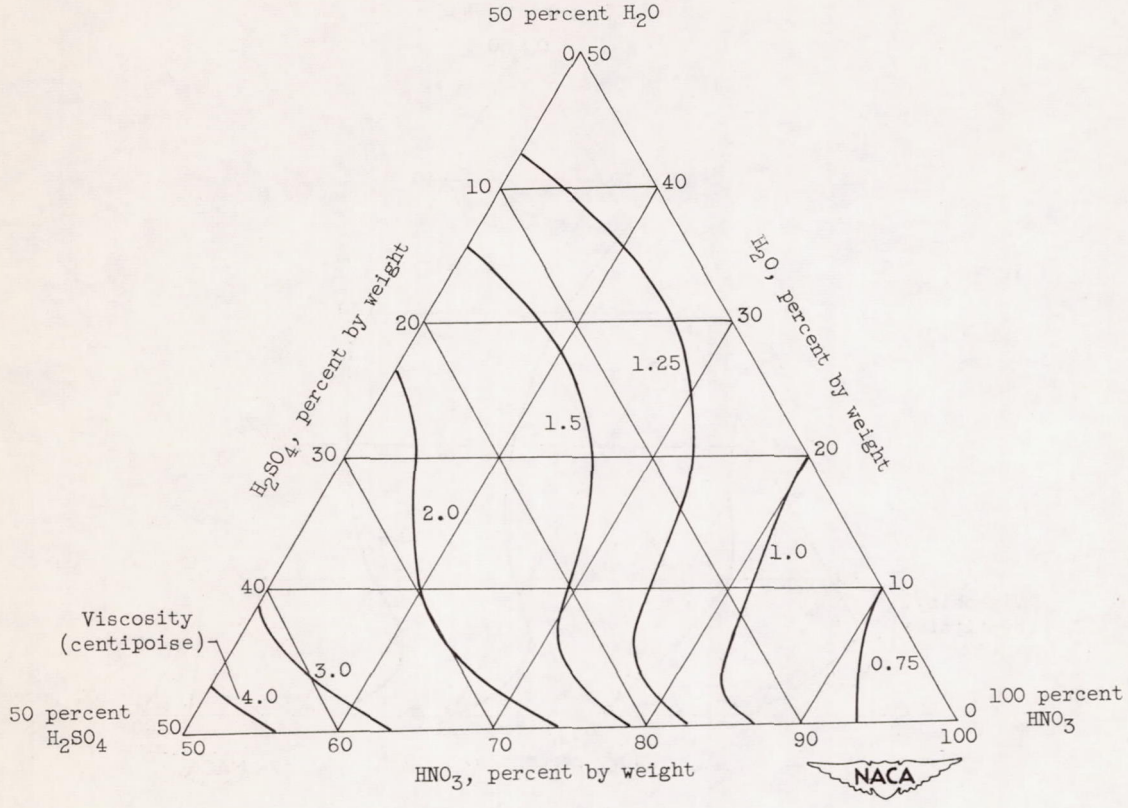

(a) Temperature, 0° C.

Figure 11. - Viscosities for $HNO_3$, $H_2SO_4$, $H_2O$ system (reference 35).



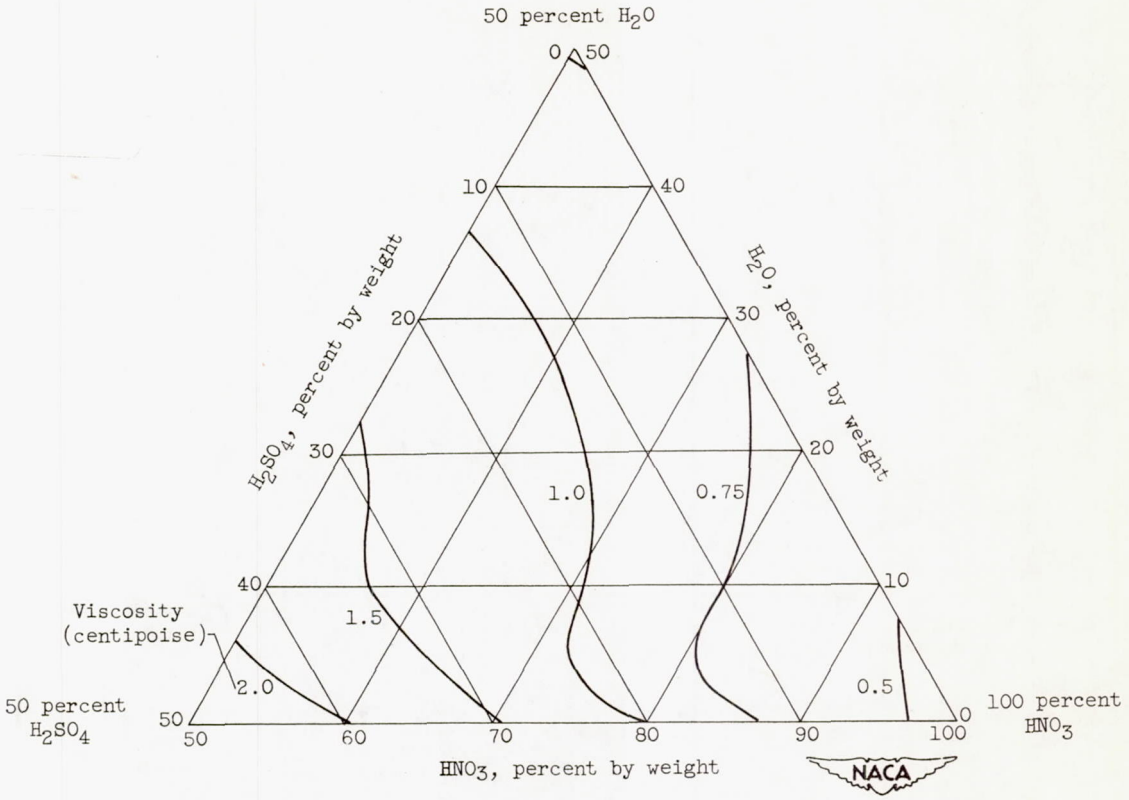

(b) Temperature, 25° C.

Figure 11. - Continued. Viscosities for $HNO_3$, $H_2SO_4$, $H_2O$ system (reference 35).




(c) Temperature, 50° C.

Figure 11. - Continued. Viscosities for $HNO_3$, $H_2SO_4$, $H_2O$ system (reference 35).




(d) Temperature, 75° C.

Figure 11. - Concluded. Viscosities for $HNO_3$, $H_2SO_4$, $H_2O$ system (reference 35).

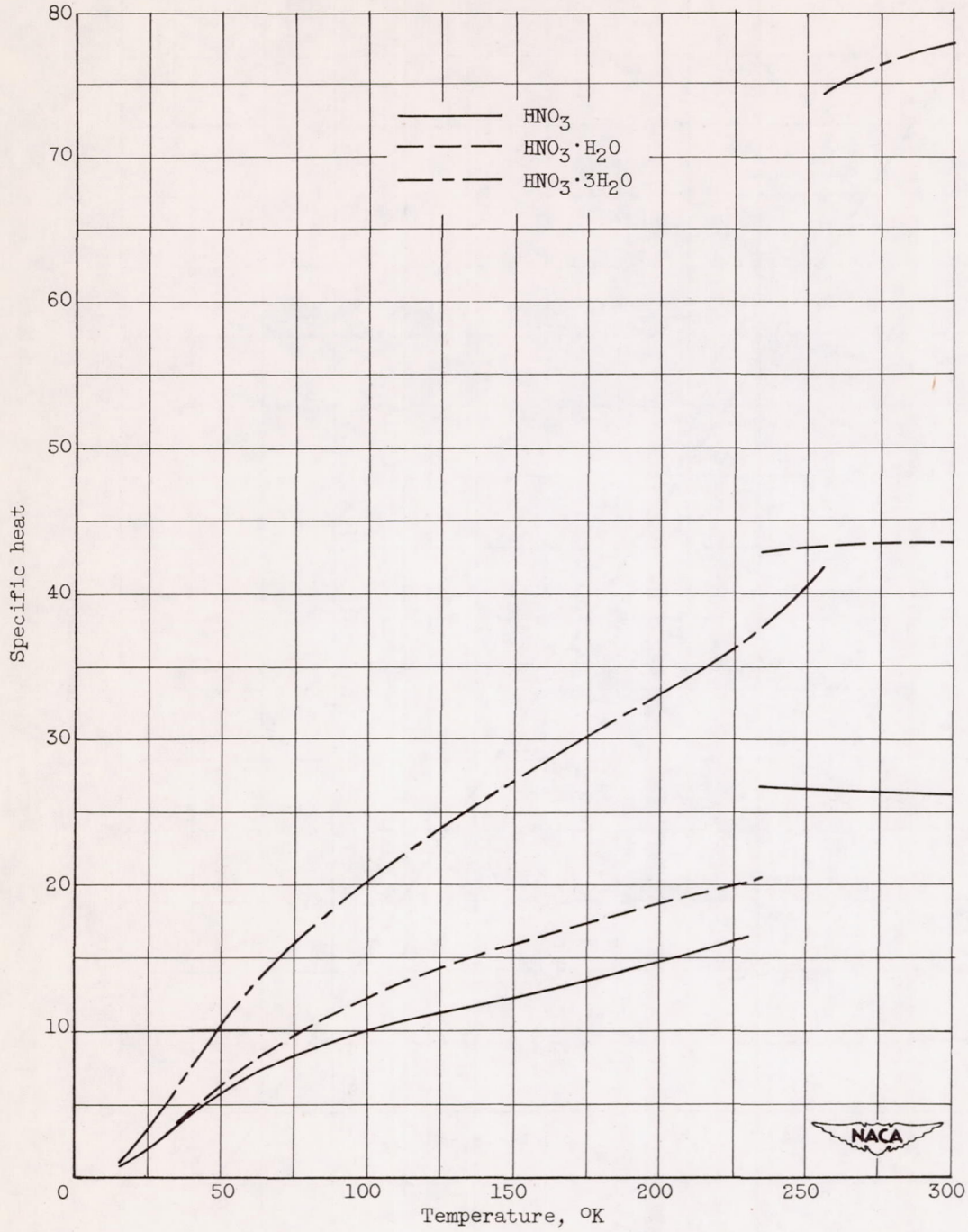



Figure 12. - Specific heats of solid and liquid nitric acid and its mono- and trihydrates (reference 22).

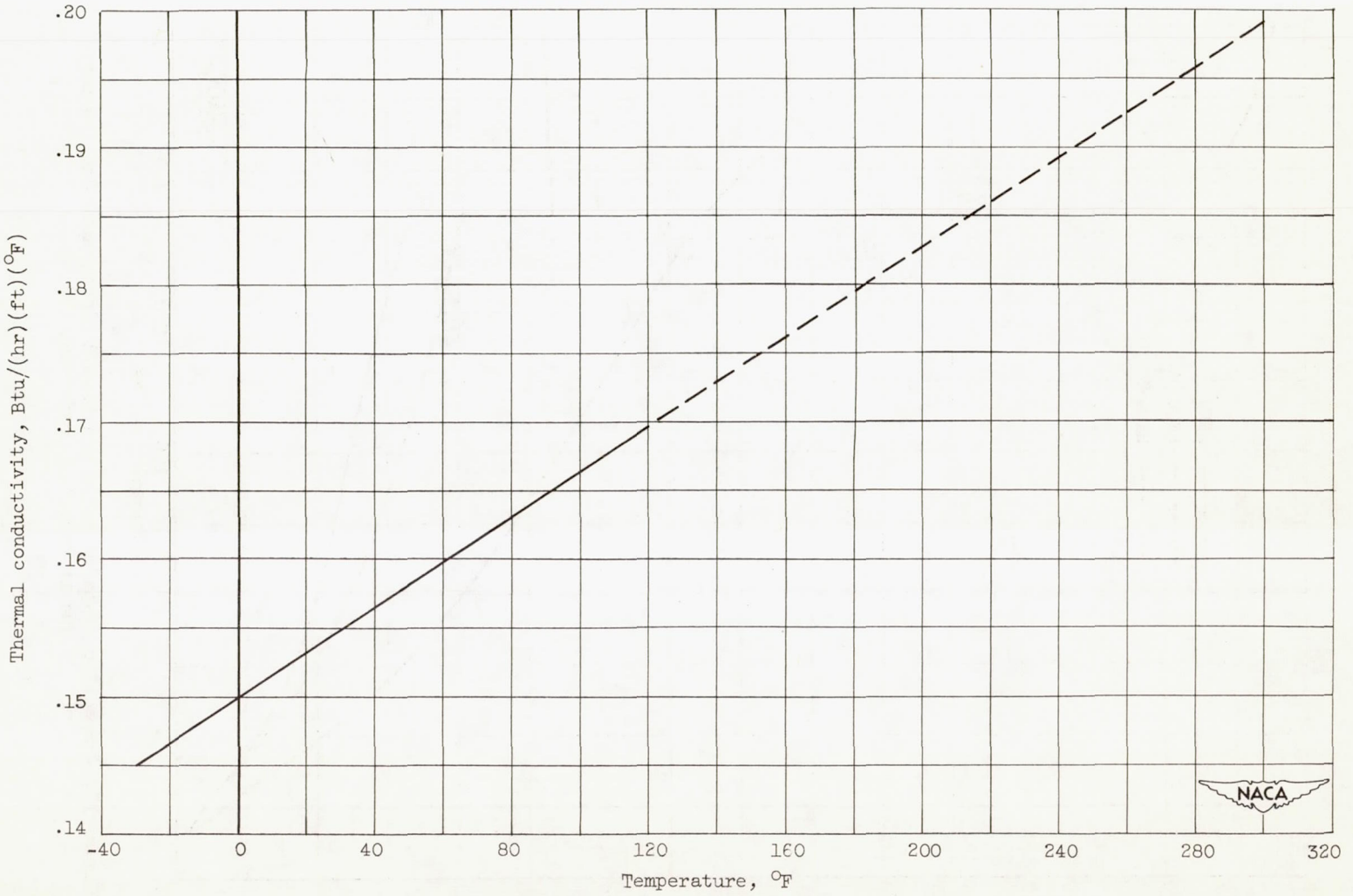



Figure 13. - Thermal conductivity of 99-percent nitric acid.

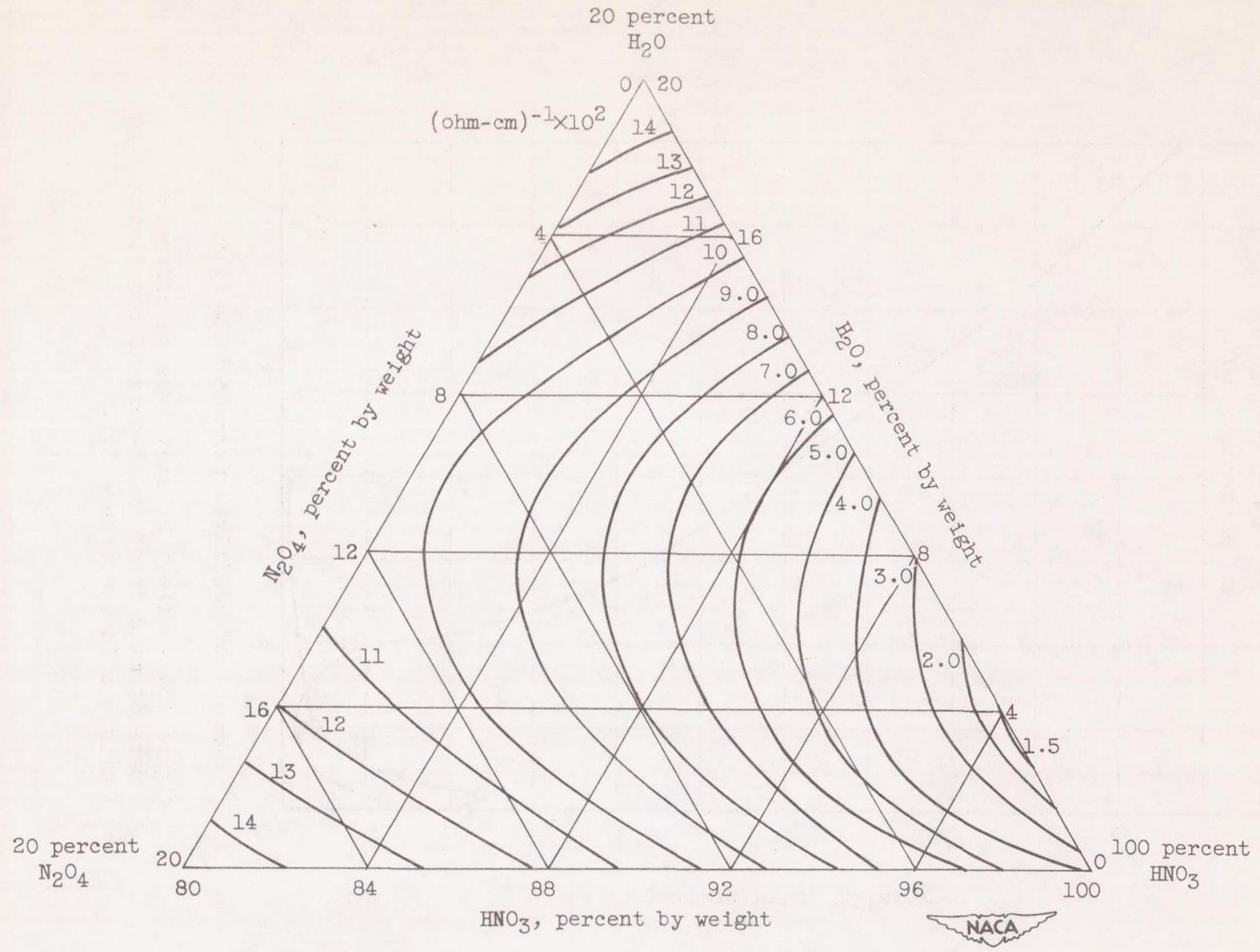



Figure 14. - Specific electric conductances at 0° C for $HNO_3$, $N_2O_4$, $H_2O$ system (reference 38).

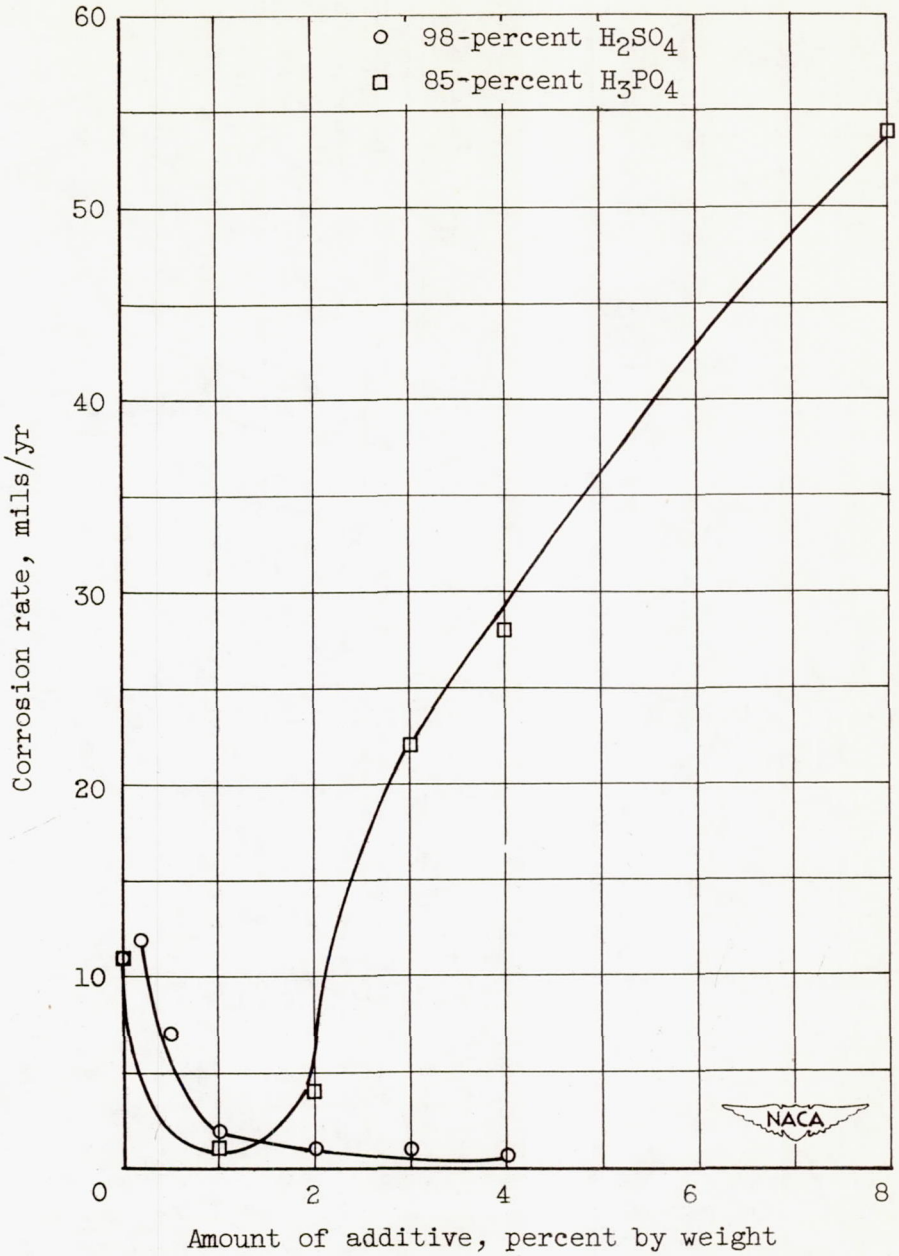



Figure 15. - Effect of additives on corrosion rate of mild steel in 16-percent red fuming nitric acid (reference 51).

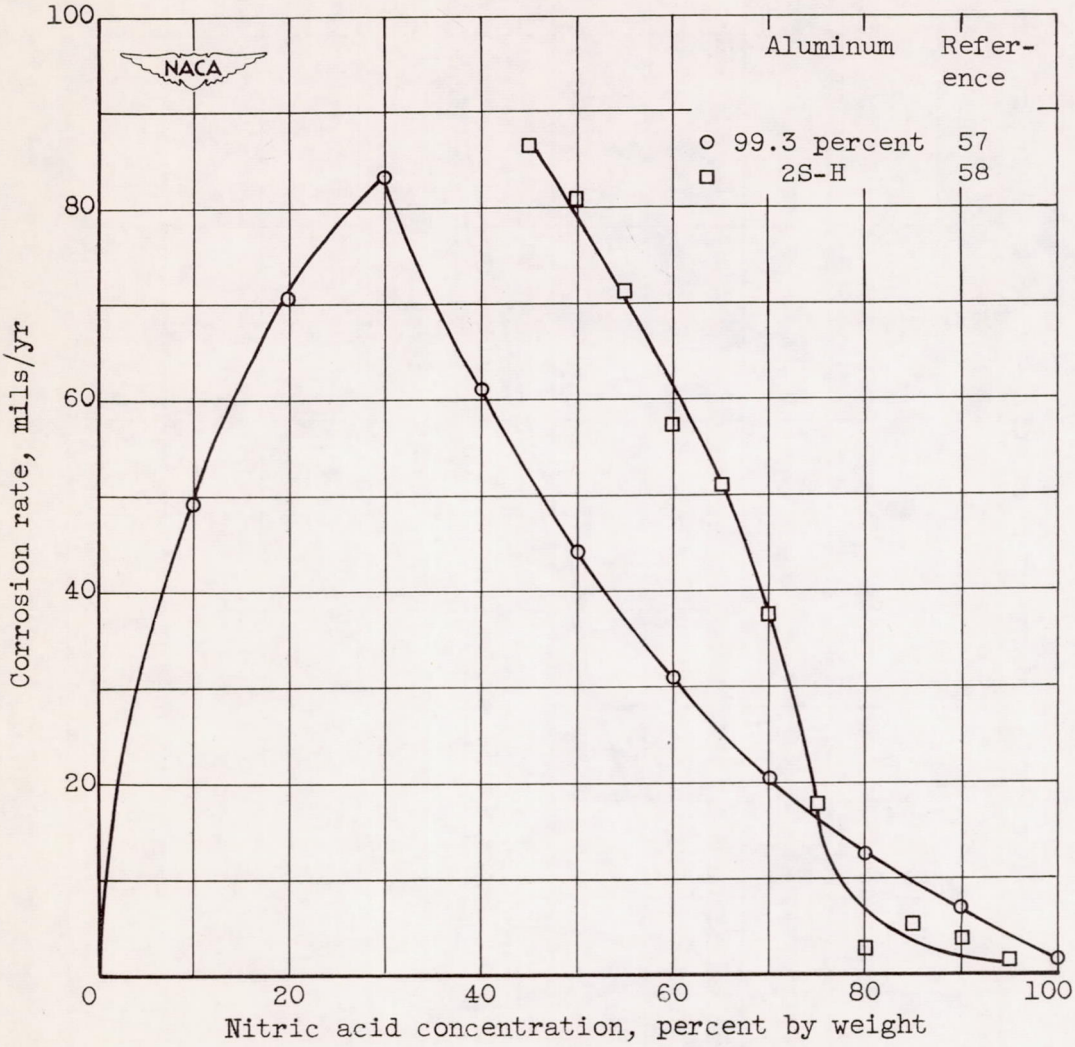



Figure 16. - Effect of nitric acid concentration on corrosion rates of 99.3-percent and 2S-H aluminum at ambient temperature.

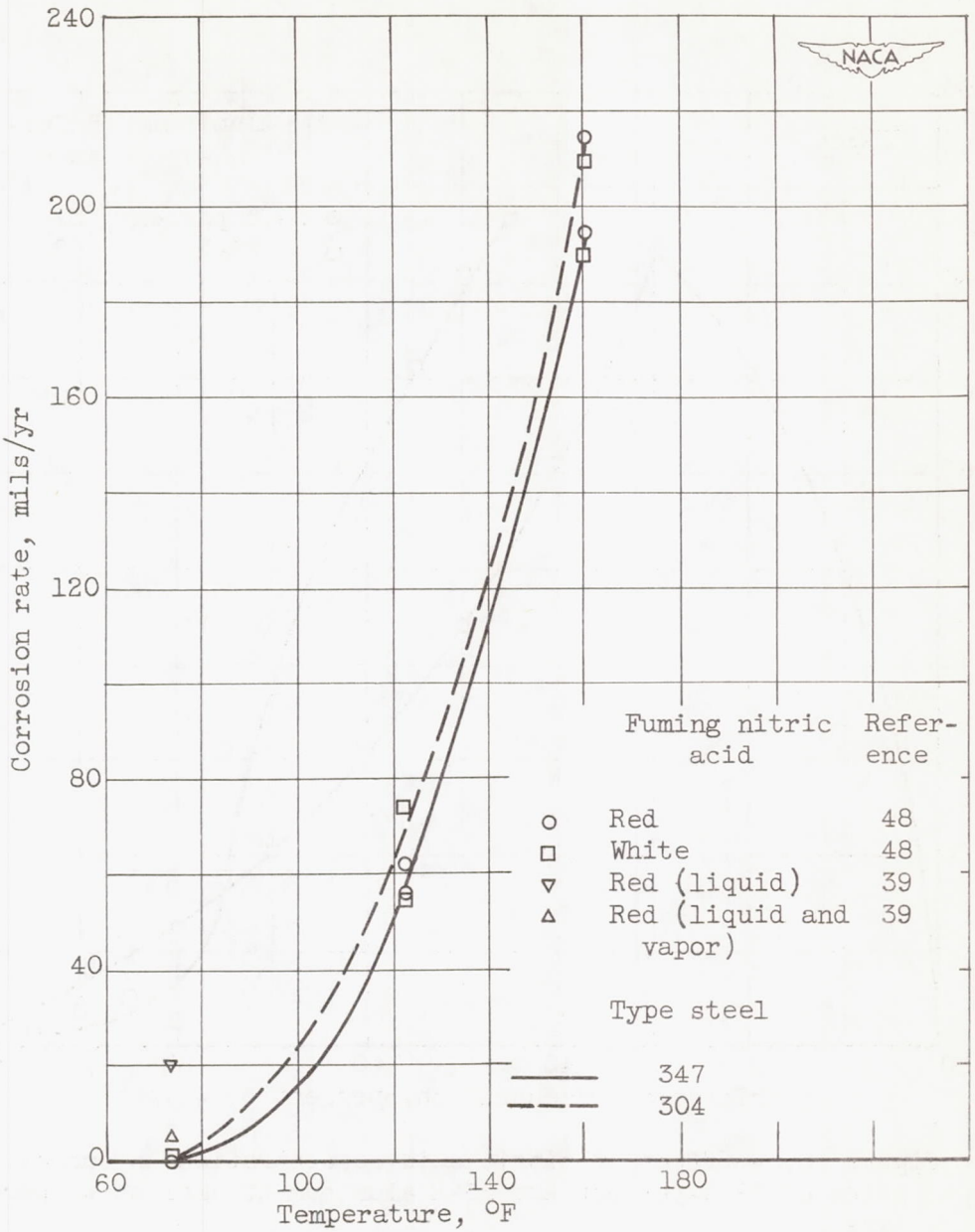
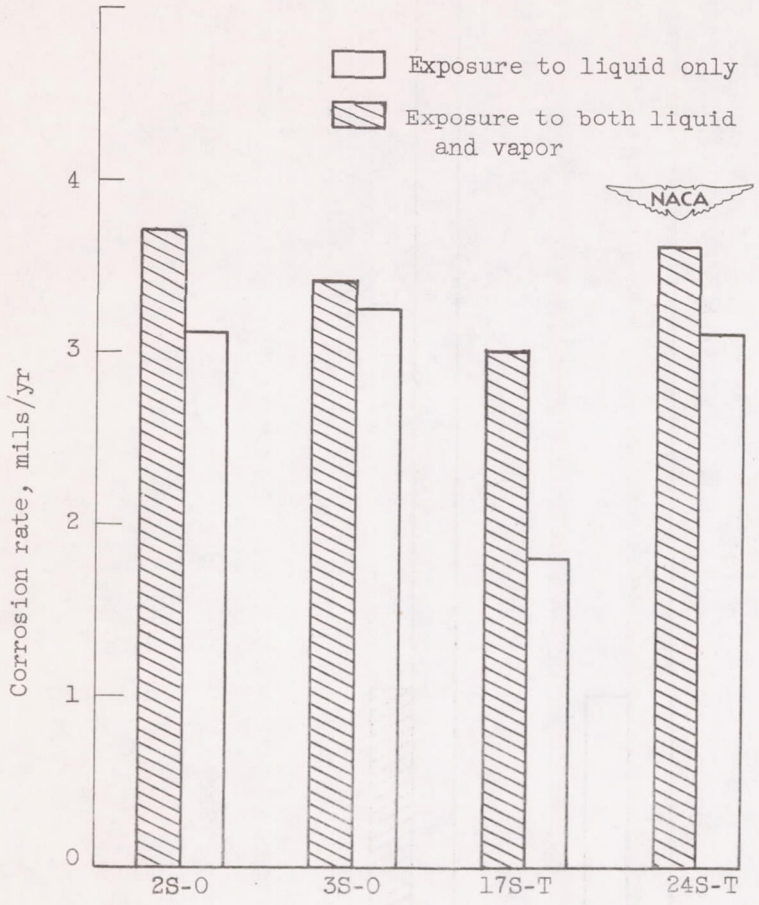
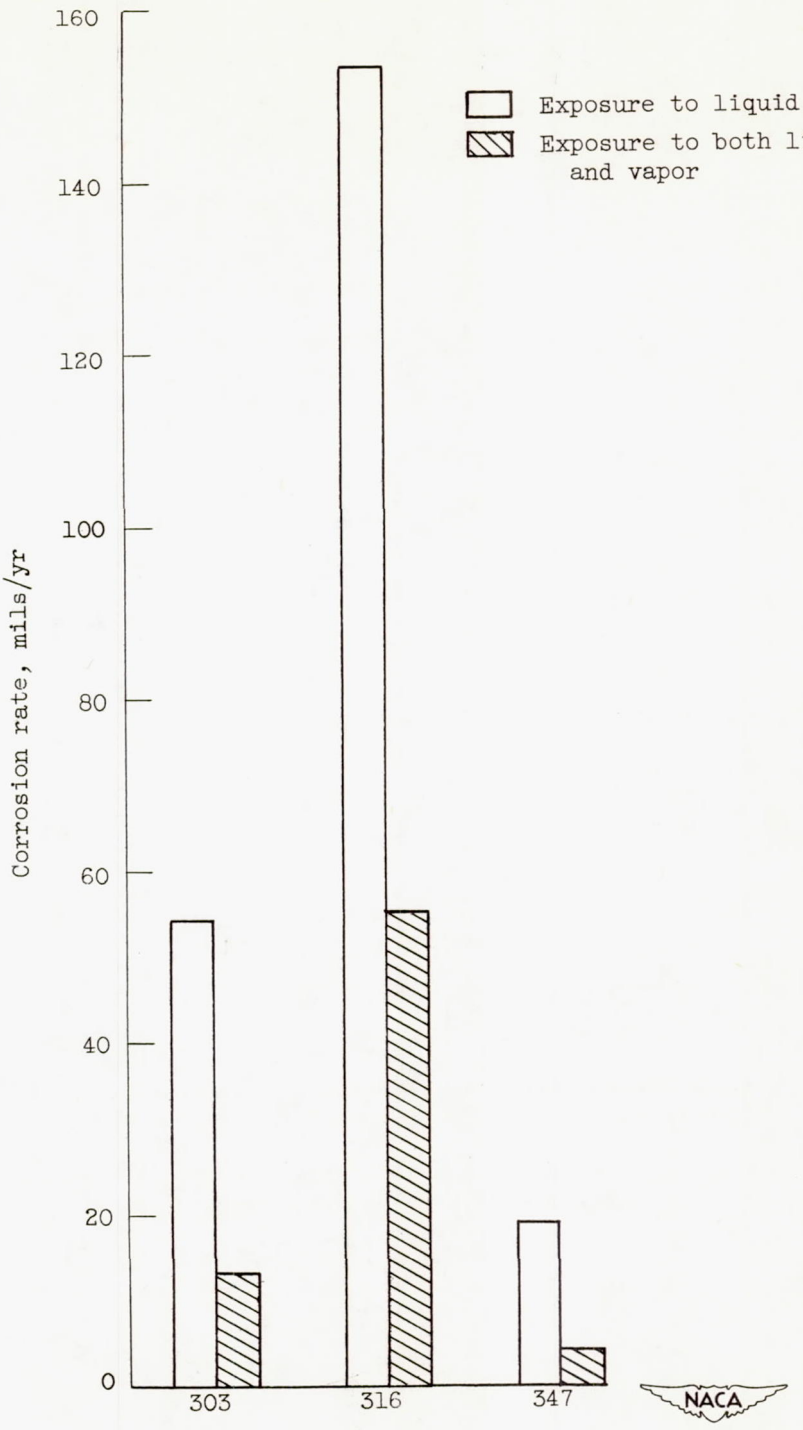



Figure 17. - Effect of temperature on corrosion rates of types 304 and 347 stainless steel in white and red fuming nitric acids.



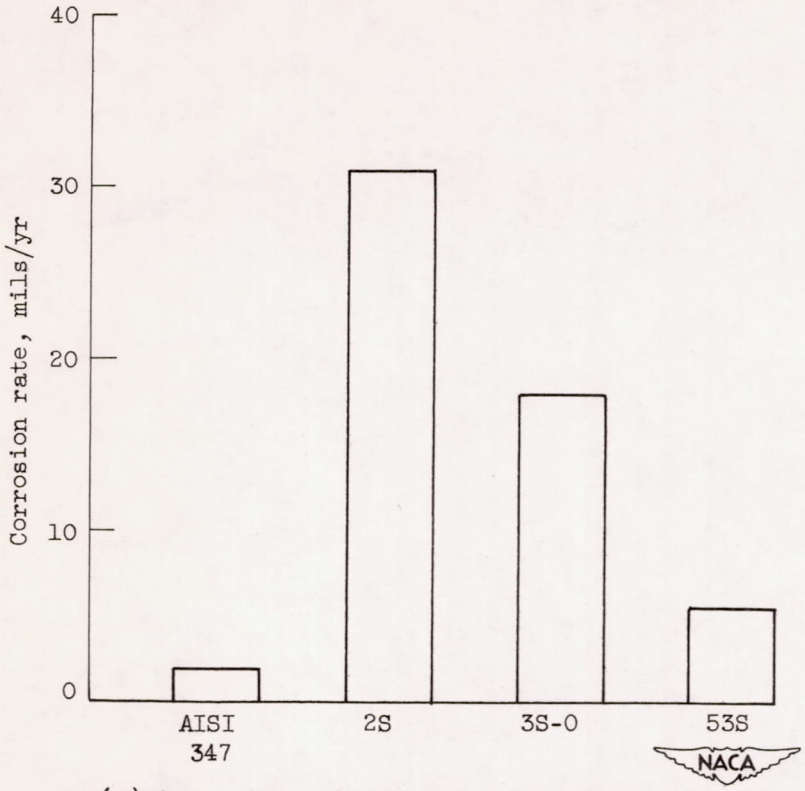

(a) Aluminum alloys in 6.5-percent red fuming nitric acid (reference 39).

Figure 18. - Comparison of corrosion rates of several alloys at ambient temperature.




(b) Several AISI type stainless steels in 6.5-percent red fuming nitric acid (reference 39).

Figure 18. - Continued. Comparison of corrosion rates of several alloys at ambient temperature.




(c) Comparison of a stainless steel with three aluminum alloys in mixed acid (reference 56).

Figure 18. - Concluded. Comparison of corrosion rates of several alloys at ambient temperature.

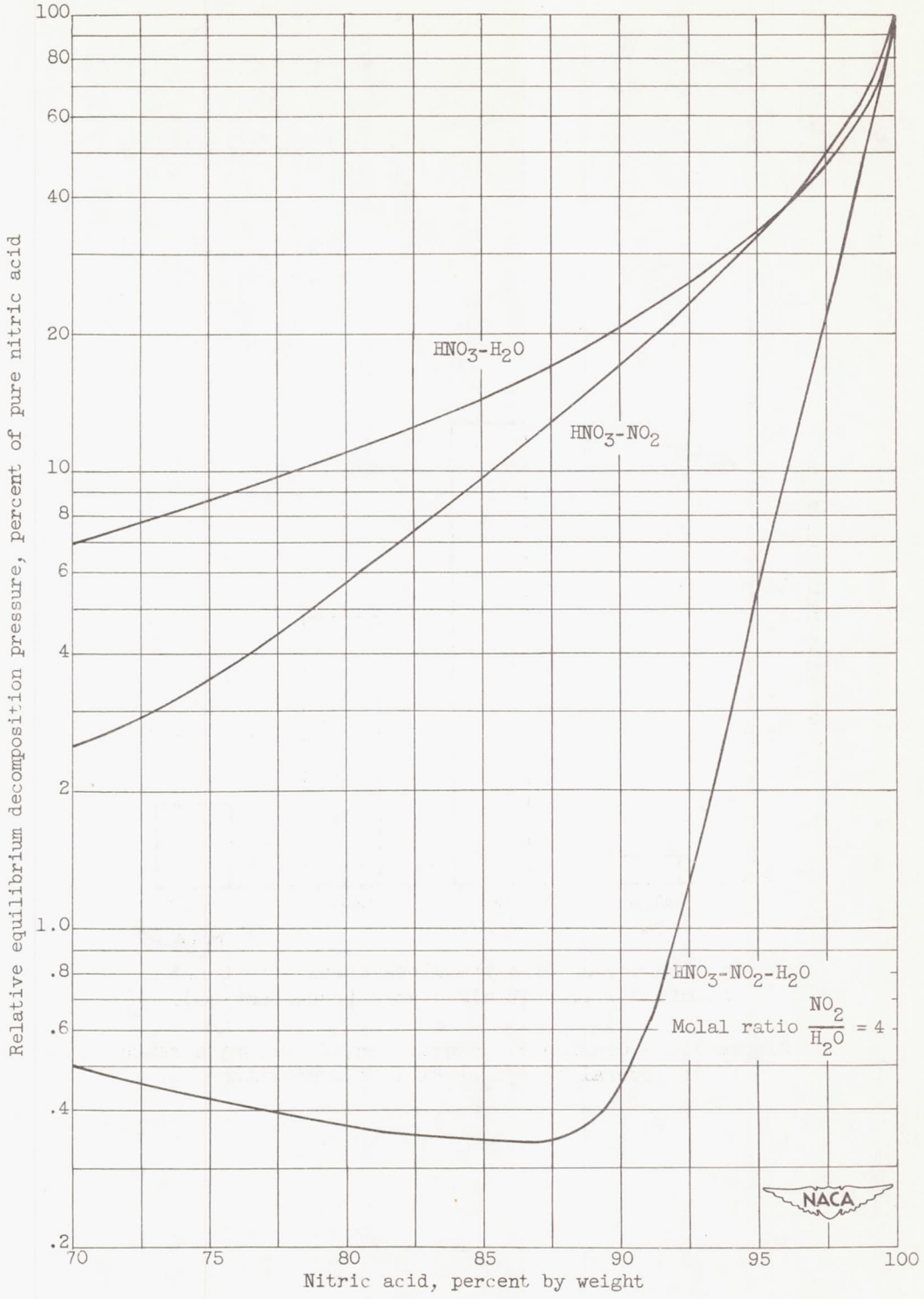



Figure 19. - Theoretical relative equilibrium decomposition pressures of nitric acid with various amounts of water and nitrogen dioxide (reference 81).

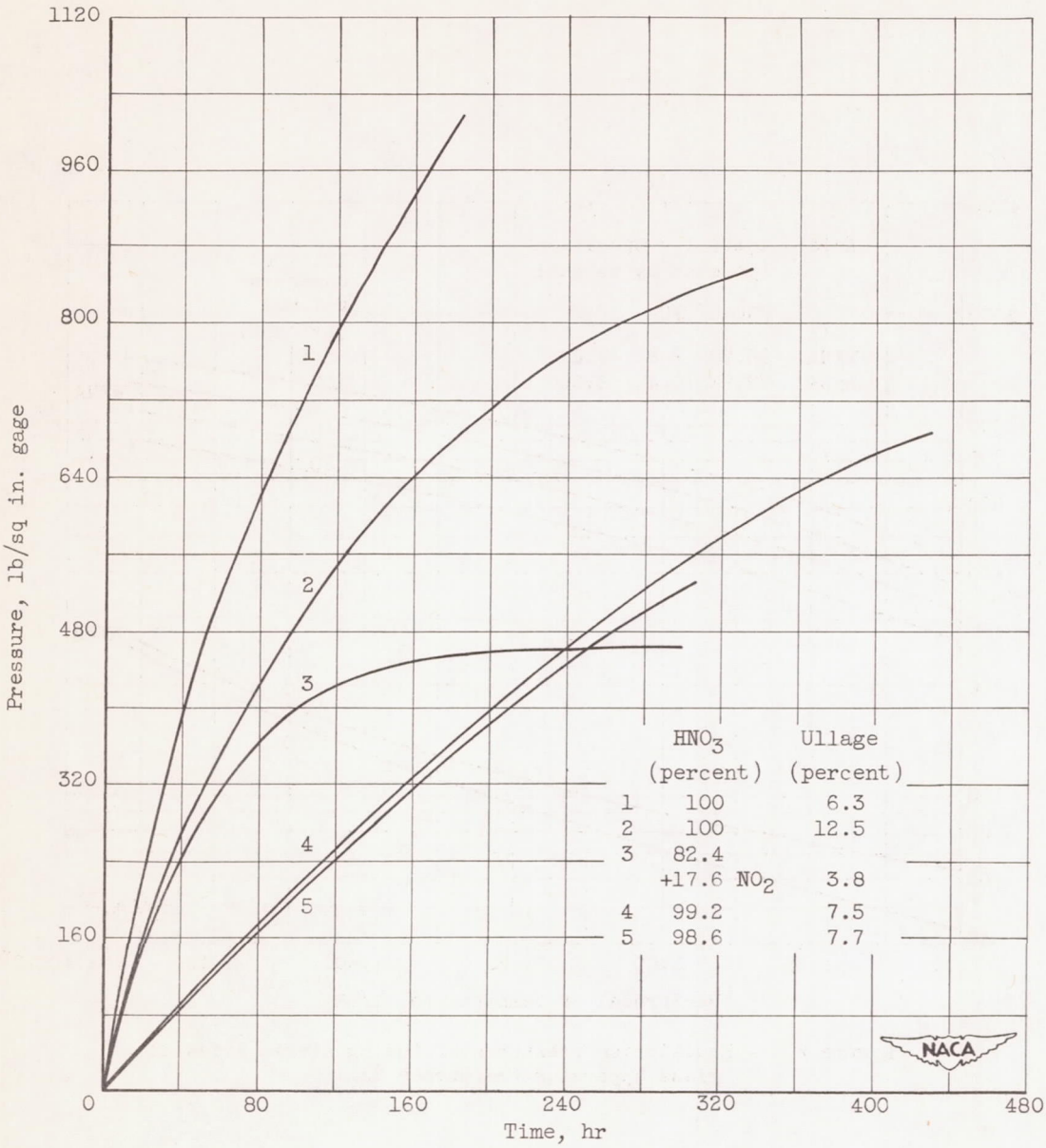



Figure 20. - Initial rates of pressure rise of several nitric acids with various ullages in glass apparatus at 122° F (reference 82).

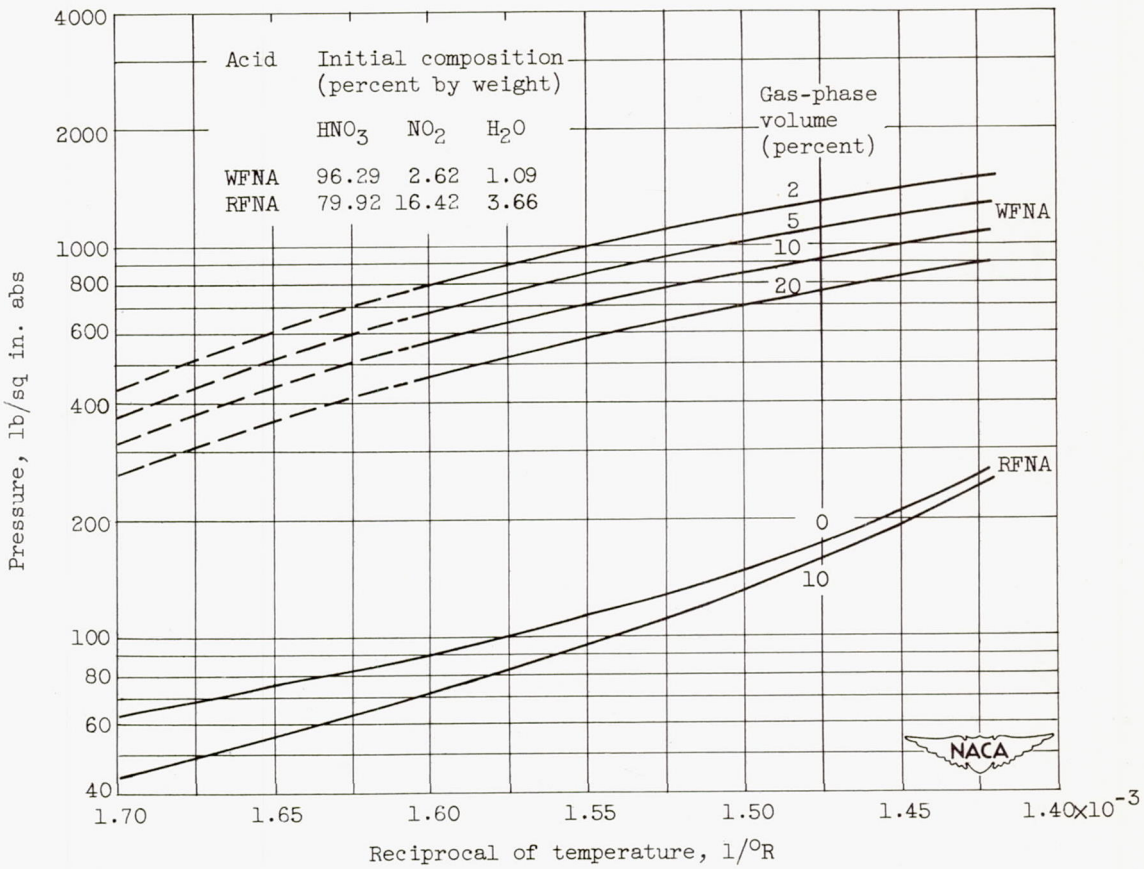



Figure 21. - Equilibrium pressures of fuming nitric acids in glass apparatus (reference 83).

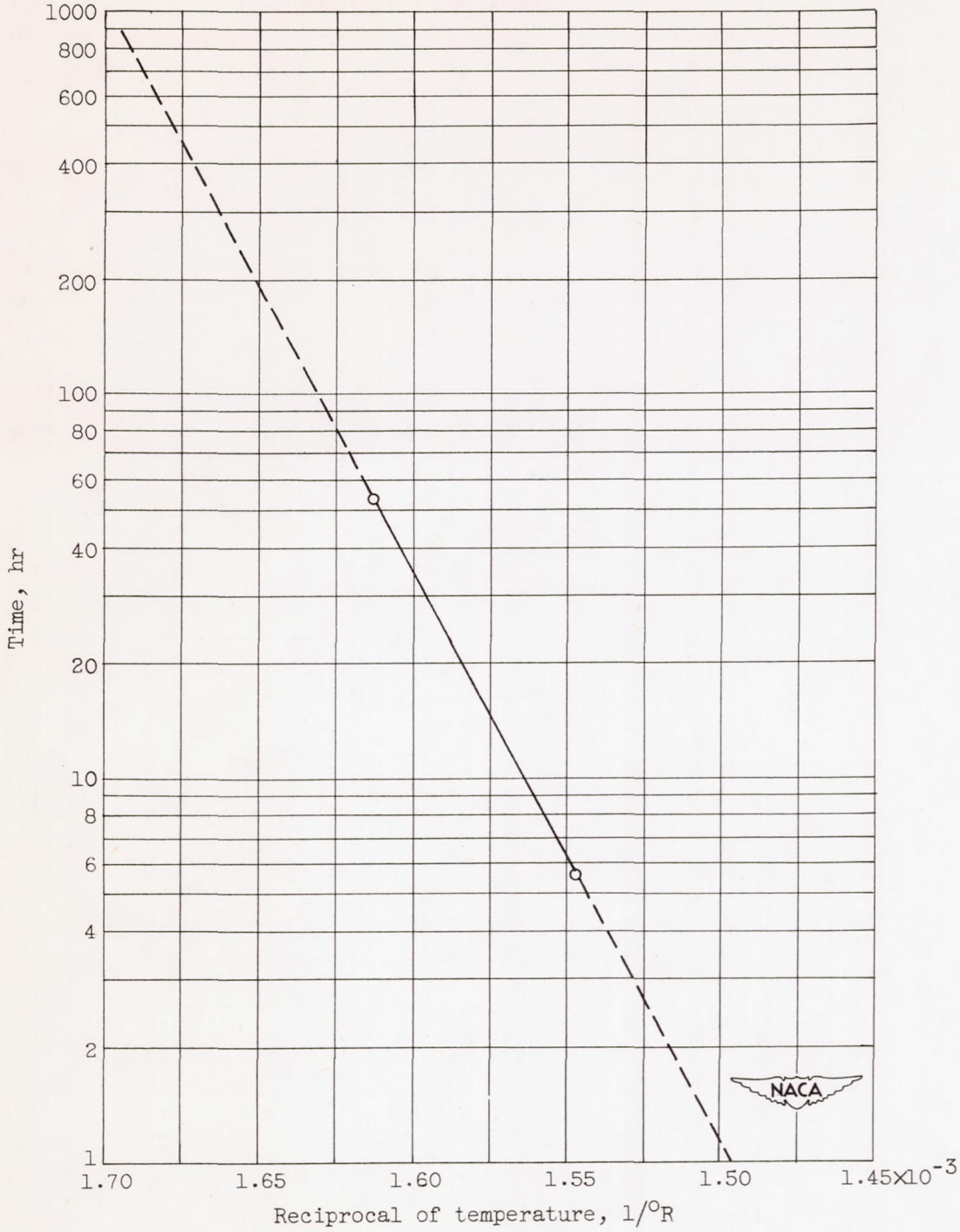
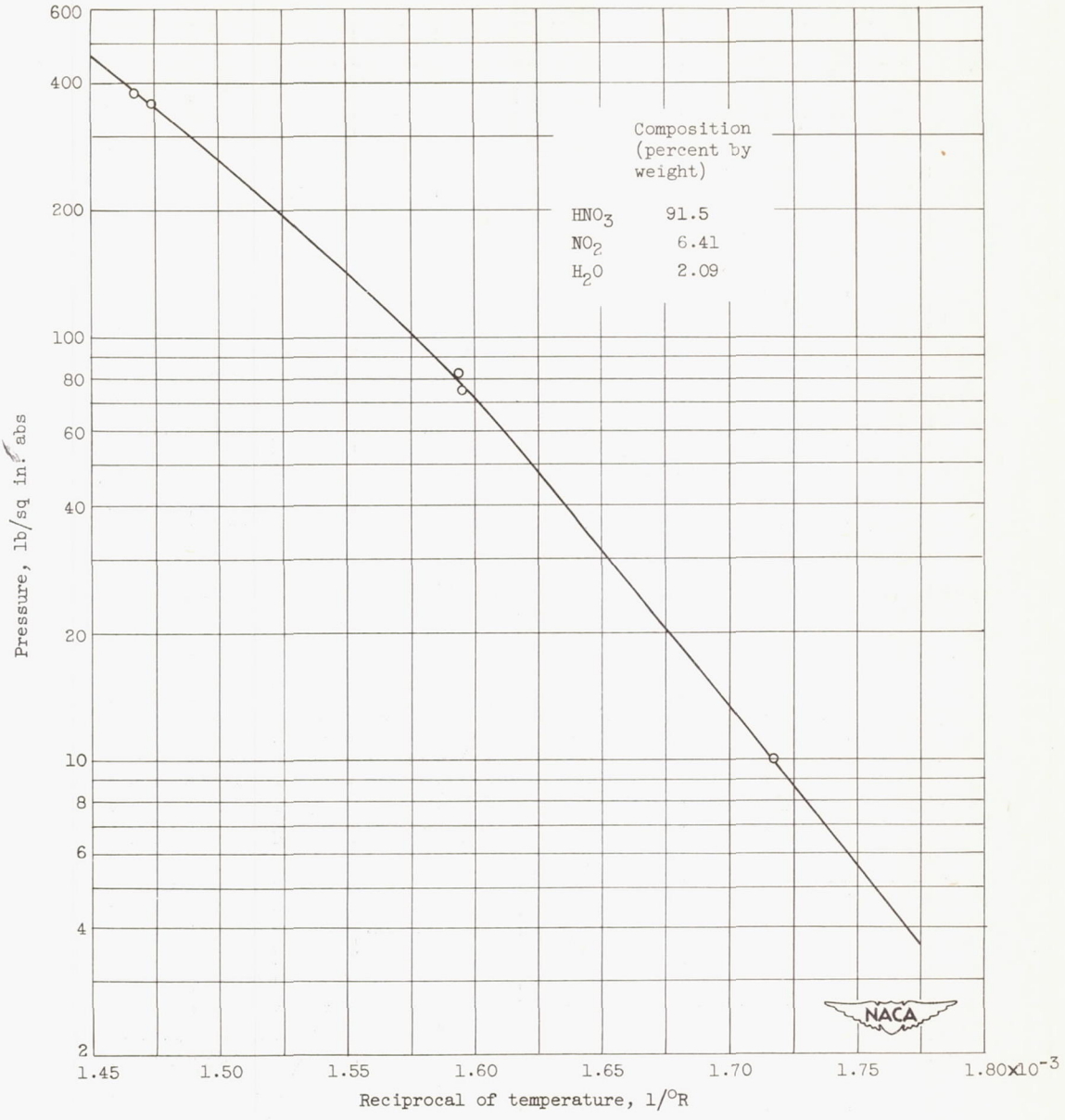
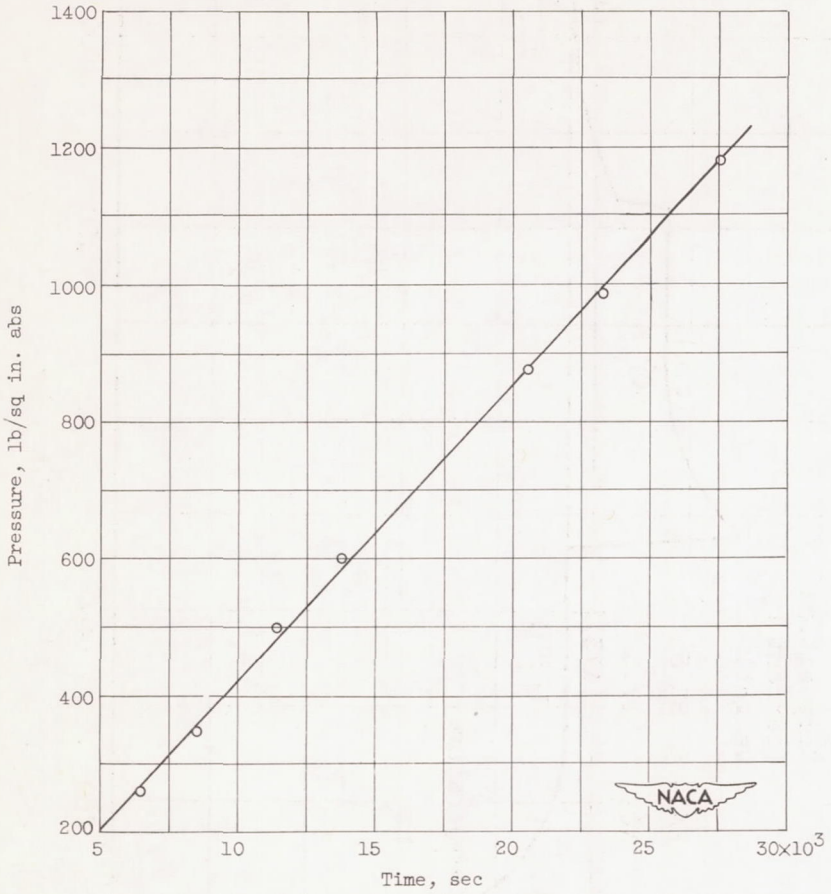



Figure 22. - Time required for white fuming nitric acid to reach equilibrium as a function of temperature (reference 83).




(a) Red fuming nitric acid (reference 84).

Figure 23. - Bubble point pressures in glass apparatus.




(b) White fuming nitric acid (reference 85). Temperature 190° F.

Figure 23. - Concluded. Bubble point pressures in glass apparatus.

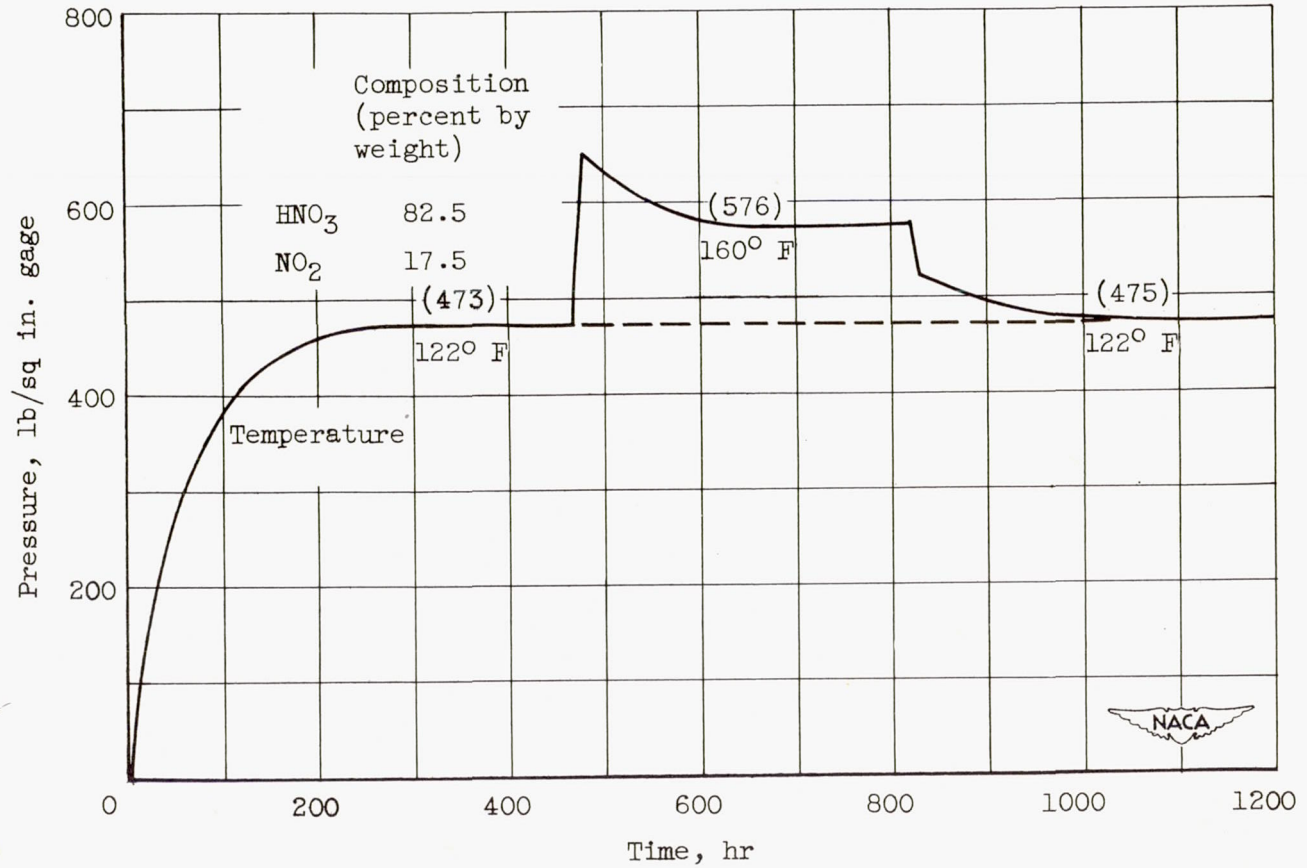



Figure 24. - Effect of a temporary temperature increase on equilibrium pressure at 122° F of red fuming nitric acid with 3.8 percent ullage (reference 82).

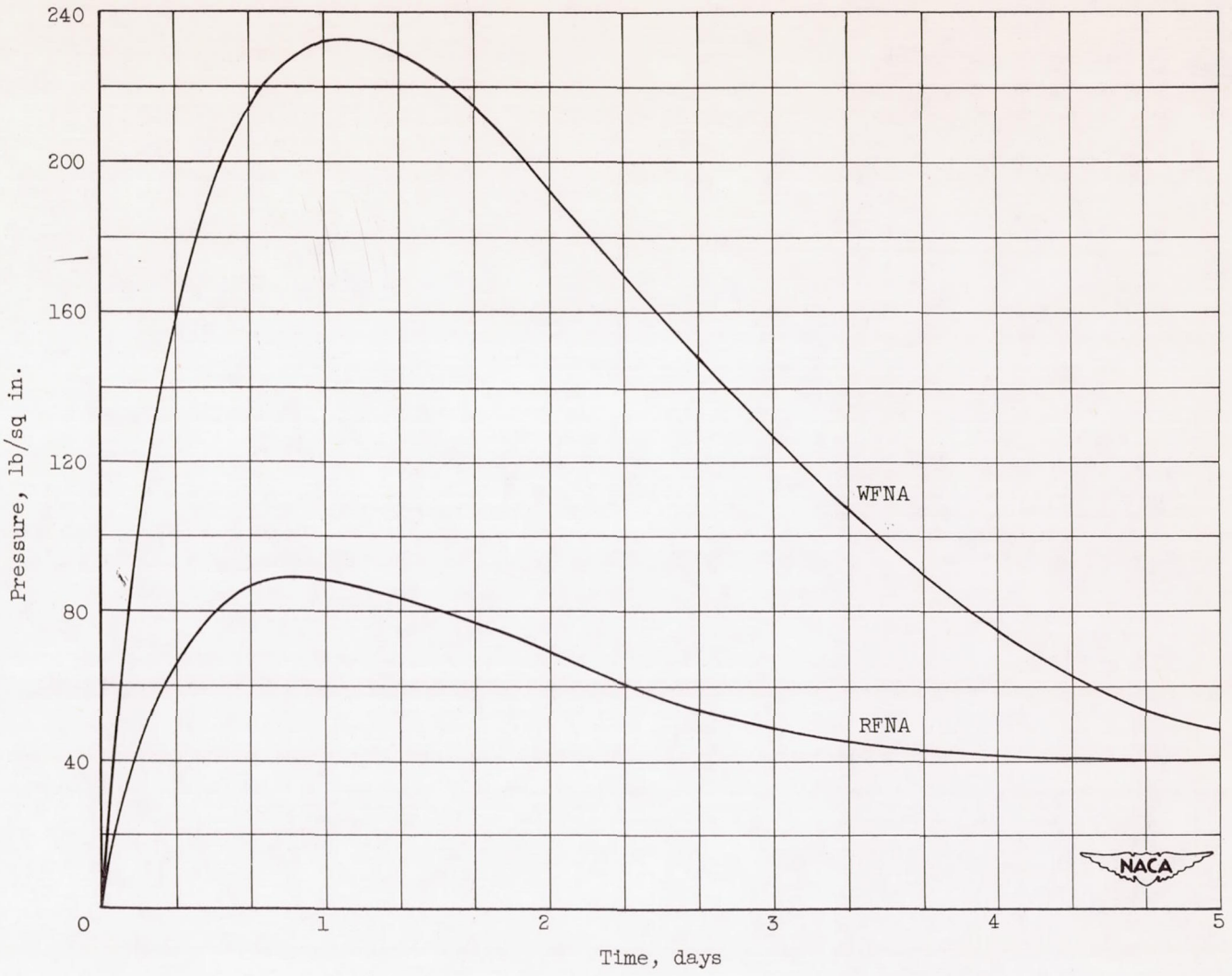



Figure 25. - Nitric acid decomposition pressures in type 347 stainless steel apparatus at 165° F with 25 percent ullage (reference 87).